SUPPRESSION OF PENTABORANE FIRES AND EXPLOSIONS

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NOTICES

FOREWORD

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ABSTRACT

The prevention of pentaborane fires and explosions in air by chemical
techniques were investigated by means of a diffusion burner and a
heterogeneous shock tube. The results indicate chemical suppression of
pentaborane-air-fires is practical. Studies on decontamination of
pentaborane were also accomplished.

This technical documentary report has been reviewed and is approved.

for MARC P. DUNNAN, Chief
Technical Support Division
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INTRODUCTION

The demand for higher performance in storable propellant systems has
led to serious consideration of pentaborane as a fuel. Pentaborane is
a powerful reducing agent which offers high performance with a variety
of conventional oxidizers, and with compounds such as hydrazine, which
are based on nitrogen. The use of pentaborane, however, poses serious
handling problems. Its high volatility and extreme toxicity make it
mandatory that residual fuel from spills or parts exposed to pentaborane
be destroyed. As a consequence of its reducing power, pentaborane is
highly reactive with oxidizers. Under a wide range of conditions, it is
spontaneously reactive with air and other common oxidizers. Consequently,
the probability of fire resulting from a pentaborane leak or spill is
very high.

A great hazard often is presented because ignition is delayed until
large amounts of propellant have accumulated; a serious explosion can
result. This possibility is especially prevalent where vapor or dis-
persed droplets from a high-pressure leak form an explosive mixture
with air. This mixture will frequently ignite spontaneously without
recourse to an external ignition source.

The simplest and, in many cases, the best means of handling a pentaborane
spill is to (1) provide for immediate ignition to eliminate the possibil-
ity of a damaging explosion, (2) stop the flow of propellant to the fire,
if possible, and (3) allow the spilled propellant to burn completely.
In many cases, however, this procedure is not practical. If pentaborane
is to be developed to its maximum potential, means must be found to reduce

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the hazards associated with fires and explosions resulting from accidental spills. Steps in the treatment of a pentaborane fire are more numerous and complex than for many other liquid fuels. Initially, it is necessary to establish control over a fire by preventing spreading to new areas and terminating local combustion. Since the fuel is pyrophoric, a means also must be found to prevent reignition once the initial treatment has served its purpose. Finally, a technique for destroying the pentaborane and freeing the affected area of the toxicity and fire hazard is required. It is also desirable that a means of preventing gas-phase explosions in enclosed compartments be available in the case of delayed ignition.

The present applied research program investigated chemical means of preventing explosions and putting out fires. The former was studied in an explosion burette, or heterogeneous shock tube, with both liquid and solid suppressants. Fire extinguishment was investigated with a diffusion burner. Extinguishants were applied in the vapor phase with the combustion air supplied to the burner. Various decontaminant solutions were evaluated in a gas evolution apparatus. Results of these studies are described.

SUMMARY

The prevention of pentaborane fires and explosions in air by chemical techniques was investigated. Two types of apparatus were employed: a diffusion burner and a heterogeneous shock tube. Water, organic liquids, and aqueous solutions were studied in the diffusion burner with a lifted flame at various pentaborane concentrations. Methyl iodide was the best material found, and was the only material which put out the flame at the higher pentaborane concentrations. A solution of iodine in carbon tetrachloride and dimethyl sulfide also showed some promise as fire extinguishants. No nitrogen compounds, phosphorus compounds, or aqueous solutions were found to show any promise.

The effects of liquid and solid suppressants on the propagation of detonations in pentaborane-air mixtures were investigated in a heterogeneous shock tube. The response of the pentaborane-air mixtures to shock initiation in this apparatus was found to be very complex. Three types of responses were noted: (1) no augmentation of the driver shock, (2) immediate amplification of the driver shock to a strong detonation wave, and (3) no amplification of the driver shock in its passage down the tube followed by an explosion outside the tube, resulting in a relatively strong detonation wave traveling in the reverse direction in the tube. The latter result was the most common; no satisfactory explanation for this behavior has been advanced. A high-surface-area, silica-alumina powder was the only material found to give significant suppression of explosion in this apparatus. This was attributed to the high surface area rather than to any chemical effect. No suppression action was observed with liquid candidates; however, a solution of potassium iodide and iodine in water exhibited a sensitizing effect. This was attributed to the presence of water, which is more volatile than the iodine and apparently masked any possible inhibition by the iodine.

The effectiveness of various decontamination solutions in destroying
pentaborane was investigated by means of the gas evolved during destruc-
tion. Decontaminants were evaluated, both by rate of gas evolution and
total gas evolved. Solutions were found which gave a wide range of
rates of gas evolution. Selection of a decontamination solution will
depend on the requirements for the specific application under consideration.

Current knowledge of the mechanisms of flame suppression has been summarized and reviewed critically by Friedman and Levy (Ref. 1, 2, and 3). These reports, together with their bibliographical sources, provide a complete survey of the theory for flames involving carbon, hydrogen, nitrogen, and/or oxygen. Combustion involving other elements is not well understood. The limited information that is available on suppression of such flames is tied closely to proposed applications for nonhydrocarbon fuels. In particular, the mechanisms of boron hydride combustion were investigated as part of the "ZIP" program. Later, Young and Eggleston (Ref. 4) studied the suppression of HEF pool fires and achieved some classification of extinguishing agents for these fuels. However, in most cases, behavior analogous to hydrocarbon fuels was inferred, and their well developed technology was heavily drawn upon. In light of the necessary reliance on hydrogen and hydrocarbon flame technology as a guide, it is well to review the key aspects of this technology.

The primary modes of operation of fire extinguishants are physical and chemical. Physical separation of fuel and oxidant, simple dilution of reactants, cooling and mechanical disturbances are typical physical contributions. Flames that propagate by means of branching chain mechanisms are subject to the effect of chemical suppressants; the additive reacts with chain carriers and acts to prevent branching. In any practical combustion problem, all of these influences will be contributing to some extent. Water has a high latent heat of vaporization and is employed principally as a coolant; however, it provides some separation and dilution as well. Although carbon tetrachloride is intended as a source of active chain-breaking species, it also must exhibit the physical modes of suppression.

When there is reason to assume a branching chain mechanism for flame
propagation, Friedman and Levy point out the marked advantage of chemical
inhibitors. If additive efficiencies are compared on the basis of weight
required to extinguish some standard, controlled fire, chemicals that
interfere with the reaction mechanism exhibit 4 to 10 times more
superiority than simple diluents and coolants. For pentaborane, then,
the following questions are of major importance:

1. Does rapid oxidation occur via a branching chain mechanism?

2. What species act as chain carriers?

3. Can common chemicals be introduced to react with carrier
   species and prevent branching?

The mechanisms of hydrogen and hydrocarbon combustion have been treated
in detail by Lewis and Von Elbe (Ref. 5). A few reactions, numbered
according to the scheme of these authors, serve to illustrate the
problem:

$$OH + H_2 \longrightarrow H_2O + H \qquad\qquad (\text{I, Ref. 5})$$

$$H + O_2 \longrightarrow OH + O \qquad\qquad (\text{II, Ref. 5})$$

$$O + H_2 \longrightarrow OH + H \qquad\qquad (\text{III, Ref. 5})$$

$$H + O_2 + M \longrightarrow HO_2 + M \qquad\qquad (\text{VI, Ref. 5})$$
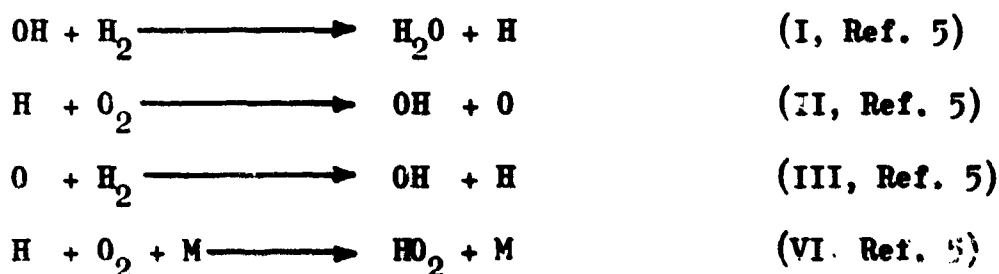
The chain carrier species are H, O, and OH. The latter is viewed as
formed directly from the reactants. Reaction I does not result in
multiplication of free radicals, but it does yield hydrogen atoms
which participate in the principal branching reaction, i.e. reaction II.
both reactions II and III multiply free radicals. Reaction VI is a chain-
breaking reaction since it removes hydrogen atoms by formation of the
stable entity HO_2 and competes with the branching reaction associated with
this species. Similar relations are proposed for hydrocarbon combustion.
The branching process can occur as follows:

$$OH + CO \longrightarrow CO_2 + H \qquad\qquad (\text{Ia, Ref. 5})$$

$$H + O_2 \longrightarrow OH + O \qquad\qquad (\text{II, Ref. 5})$$
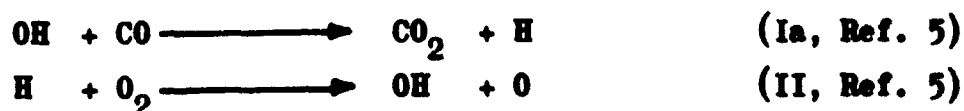
Here, the hydroxyl radical reacts to yield a hydrogen atom that, in turn, produces a new hydroxyl radical and an oxygen atom. Thus reaction II is a branching reaction for these reactants, also, and the hydroxyl radical is a key chain carrier.

Rosser, Inami, and Wise (Ref. 6) have applied these mechanisms to the problem of chemical combustion inhibitors. They extended earlier observations of the inhibiting effects of halogen compounds on hydrocarbon combustion and proposed a mechanism which includes the halogen acids as intermediates, i.e.,

$$OH + HX \longrightarrow H_2O + X \qquad (1)$$

$$H + HX \longrightarrow H_2 + X \qquad (2)$$
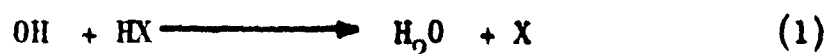
In this way, the chain carriers are replaced by halogen atoms and branching is slowed. The halogen acid is regenerated by

$$H\alpha + X \longrightarrow HX + \alpha \qquad (3)$$

where α is an organic fragment, e.g., alkyl radical. Rosser et al. report, further, that noncarbon-containing systems can be inhibited if chain branching occurs. They cite the ammonia-air flame as an example. Finally, they note that flames incorporating nitrous oxide or nitrogen dioxide are not subject to chemical inhibition. This is understood on the basis of thermal processes as opposed to the chain branching in oxygen oxidations.

Covalent halogen compounds are found to have good fire suppressant qualities. Two general statements, although far from rigorous, are a useful guide to the relative efficiencies of these compounds. First, the greater the number of halogen atoms in the parent molecule the higher the efficiency and, second, the halides are ranked relative to each other in the sequence iodine > bromine > chlorine $\geq$ fluorine. A practical review of these considerations may be found in Belles (Ref. 7).

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The role of powders and ionic salt solutions as combustion inhibitors
is comparable to that of covalent halides. Suppressant efficiency is
a function of composition and, in the case of powders, particle size.
The first comprehensive research on salt solutions, related especially to
aqueous solutions of alkali-metal compounds, was carried out by Thomas
and Hochwalt (Ref. 8). Broader study led to the conclusion that chain-
breaking contributions were a property of alkali and alkali-earth
cations. Particular attention has been focused on the unpredictable
effect of anions without appreciable success. In the special case of
aluminum chloride, Levy and Friedman (Ref. 9) propose extinction of
of hydrocarbon fires through vaporization and chemical reactions similar
to those of chlorine and carbon tetrachloride. Willbourn and Hinshelwood
(Ref. 10) and Lewis and Von Elbe investigated the effect of salt-coated
container walls on the explosion limits of hydrogen and oxygen. Cations
of the above type with a variety of anions, both halide and nonhalide,
were found to be effective. The former researchers suggested the follow-
ing chain-breaking action:

$$KX + H \longrightarrow K + HX \qquad (4)$$
$$KX + H \longrightarrow KH + X \qquad (5)$$
$$K + X \longrightarrow KX \qquad (6)$$
$$KH + HX \longrightarrow KX + H_2 \qquad (7)$$

Most recently Friedman and Levy (Ref. 11) studied the effect of potassium
vapor on the methane-air diffusion flame. Alkali-metal vapor was
introduced with the methane and had no inhibiting effect at concentrations
which are within the region of powerful inhibition by organic bromides.
They propose a mechanism for the cations noted earlier in conjunction
with oxygen-containing anions

$$KOH + H \longrightarrow H_2O + K \qquad (8)$$
$$KOH + OH \longrightarrow H_2O + KO \qquad (9)$$
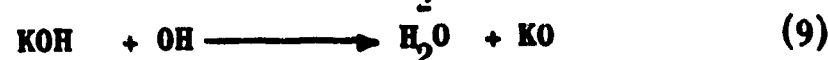
which accounts for removal of H and OH chain carriers by the gaseous
hydroxide.

The work of Laffitte and Bouchet (Ref. 12) on explosion waves in gaseous mixtures suggested a chemical role for powder suppressants. They observed that most salts exhibited comparable efficiencies for deflagration extinction when small particle sizes were employed. A fine powder provides extensive surface on which recombination can occur. It appears probable that, when sufficient surface is available, the nature of the surface and attendant third-body efficiency is unimportant. However, compositional effects appeared in deflagration suppression with larger particle sizes and in instances when the combustion reaction attained detonation velocities.

It is apparent that a method of chemical inhibition of pentaborane oxidation should be sought. To begin, some form of reaction mechanism must be selected as a basis of attack. The bulk of the work on boron hydride oxidation and pyrolysis kinetics and mechanisms was carried out at Rensselaer Polytechnic Institute under ZIP program support. Price (Ref. 13) studied the effect of diluent gases on the first and second explosion limits of diborane and oxygen mixtures. He observed that oxygen was 150% more effective than hydrogen and 50% more effective than nitrogen. Whatley and Pease rejected the possibility of a reaction between either diborane or the borane radical and oxygen (Ref. 14). They deduced a thermal mechanism for diborane-oxygen explosions. Roth (Ref. 15) continued the study of the second explosion limit of diborane. His data supported a branching chain mechanism and he proposed the following reactions:

$$BH_3 + O_2 \longrightarrow BH_2OH + O \tag{10}$$

$$O + B_2H_6 \longrightarrow BH_2OH + BH_3 \tag{11}$$

$$BH_2OH + B_2H_6 \longrightarrow B_2H_5OH + BH_3 \tag{12}$$

$$BH_3 + O_2 + M \longrightarrow HBO_2 + H_2 + M \tag{13}$$

$$BH_3 + B_2H_6 \longrightarrow B_3H_7 + H_2 \tag{14}$$
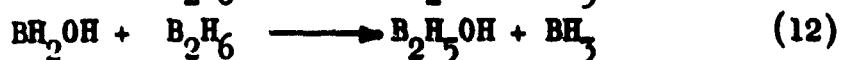
where reaction 10 is the primary branching reaction and reaction 13 is the chain-breaking step. The efficiencies of various third bodies in

reaction 13 are used in explanation of Price's results. Later publications by Roth and Bauer (Ref. 16) and Fehlner and Strong (Ref. 17) support a bimolecular chain-branching and trimolecular chain-breaking mechanism. The efficiencies of nitrogen, argon, and helium in reaction 13 are shown to be in good agreement with collision theory. Bragg, McCarthy, and Norton (Ref. 18) found the pyrolysis of diborane to be of order 1.5 with an activation energy of about 25 kilocalories per mole. The initial reaction was considered to be

$$B_2H_6 \longrightarrow 2BH_3 \qquad (15)$$

Reaction 15, together with reactions 10 through 14, form a complete picture of diborane oxidation.

Ludium (Ref. 19) observed mixtures of tetraborane and oxygen and proposed a chain-branching reaction for this oxidation, also. He found lead tetraethyl inhibited the reaction erratically and, in some cases, prevented explosion entirely. Snyder (Ref. 20) investigated the explosive reactions of decaborane in oxygen. He proposed a chain scheme similar to that for diborane, i.e.,

$$B_{10}H_{14} + O_2 \longrightarrow B_9H_{11} + BH_2OH + O \qquad (16)$$
$$B_9H_{11} \longrightarrow B_4H_4 + B_5H_7 \qquad (17)$$
$$B_{10}H_{14} + O \longrightarrow B_4H_4 + B_5H_7 + BH_2OH \qquad (18)$$
$$B_5H_7 + O_2 \longrightarrow B_4H_4 + BH_2OH + O \qquad (19)$$
$$B_5H_7 + O_2 + M \longrightarrow B_5H_7O_2 + M \qquad (20)$$
$$BH_2OH + O_2 \longrightarrow HBO_2 + H_2O \qquad (21)$$

where reactions 18 and 19 are chain branching and reaction 20 is the breaking step. Nitrogen exhibited a broadening effect on the explosive peninsula, indicating a lower chain-breaking efficiency than for oxygen or decaborane. Nitrogen dioxide sensitized the reaction, while iron pentacarbonyl inhibited it, tending to confirm the importance of oxygen atoms to the reaction mechanism. Finally, Baden, Bauer,

and Wiberly (Ref. 21) report that pentaborane oxidation is a branched chain reaction. Explosion limits are shifted by reaction products and are sensitive to vessel size as well. The oxidation is inhibited, at room temperature, by iron pentacarbonyl; this result is attributed to the destruction of carrier oxygen atoms. Maximum variation in explosion limits is achieved with a carbonyl concentration of 0.1 to 1.0%.

In general, the oxidation reactions of the lower boron hydrides appear to proceed by means of branching chain mechanisms. Key carrier species include borane and higher borane radicals, e.g., B_5H_7, as well as oxygen atoms. In common with the methods of extinguishing hydrogen and hydrocarbon flames, the most efficient technique should be chemical through restriction of radical multiplication. In the former cases, covalent halogen compounds are effective in reactions with chain-carrying hydrogen atoms and hydroxyl radicals. For pentaborane, the approach of reaction with oxygen atoms to restrict branching seems promising. The difficulty in this technique will rest with the reactivity of borane radicals and the likelihood of substituting one branching process for another.

Some further guidance can be found in the limited literature on boron hydride flames and fire suppression. Spontaneous ignition limits for pentaborane were studied by Schalla of NACA (Ref. 22). She found a lean limit of 14-mole% pentaborane at 25 C and 1 atmosphere. No rich limits could be identified; the addition of air to pentaborane vapor gave ignition, to pressures as low as 2 mm Hg at 23 C. Of interest was the observation that air introduced below the surface of liquid pentaborane resulted in explosions only in the vapor space above the liquid.

A number of researchers have studied diborane flames. Parker and Wolfhard (Ref. 23) observed that the addition of ethane to diborane and oxygen significantly extends the mutual flammability limits beyond the limits predicted from data for the pure fuels. Burning velocity is a maximum for a stoichiometric mixture of diborane and oxygen; the addition of hydrocarbon reduces the burning velocity. Kurz studied the effect of

diborane on propane-air premix flames (Ref. 24). For diborane in small amounts, i.e., lean flames up to 20% diborane in the fuel and rich flames up to 6% diborane in the fuel, the flame speed of the mixture is less than that for pure propane. In rich flames, containing over 6% boron hydride, the flame speed of propane is exceeded; diborane is burned selectively and a two-step flame results. Berl and Dembrow (Ref. 25) report two-stage flames, also. The diborane burns more rapidly and, when some oxidizer remains, a secondary hydrocarbon flame takes hold. Berl, Gayhart, Maier, Olsen, and Renich (Ref. 26) report on laminar premix flames of pentaborane, oxygen, and nitrogen. Maximum burning velocity was found on the slightly fuel-rich side of stoichiometric. The burning velocity for a mixture with the oxygen-nitrogen ratio of air is over 100% greater than the maximum burning velocity of hydrogen in air. Also, the flame speed is very sensitive to oxygen concentration.

Very limited systematic study of boron hydride fire suppression is reported in the literature. Much of the existing knowledge has been communicated informally, is highly qualitative, and is closely related to the immediate production or application problem of the reporting agency. George (Ref. 27) compared the efficiencies of common fire extinguishants on diborane, ethane, and hydrogen fires. Carbon dioxide and nitrogen were poor extinguishants for diborane and succeeded only in transferring the flame to a point of higher oxygen content. Under identical conditions, ethane and hydrogen fires were quickly extinguished. Carbon tetrachloride was effective on ethane, ineffective on hydrogen, and resulted in a continued, smoke-generating reaction with diborane. Steam was ineffective on diborane, while water was the most successful of the extinguishants tested. Sand and sodium bicarbonate suppressed diborane fires only after application in considerable depth.

Young and Eggleston studied fires of propylpentaborane (HEF-2) and ethyldecaborane (HEF-3). Their basis of comparison was a pool fire of constant fuel level. Commercial dry chemicals, water sprays, carbon dioxide, and nitrogen were ineffective against HEF-2 fires. Fuel complexing agents, including formaldehyde and several amines, showed some tendency toward reducing the intensity of the same fires. However, as the

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increasing amine concentration began to give some promise, the limit of flammability of the amine was attained. Aqueous salt solutions either were ineffective or actually promoted more rapid burning. Halogen compounds were not studied because of shock sensitivity data reported by Olin Mathieson Chemical Co. In an unreferenced report of the latter company, carbon tetraiodide and isopropylchloride were claimed to be insensitive. On the other hand, carbon tetrachloride, chloromethyl ether, dibromoethane, dichloroethane, methylene chloride, and fluorotrichloromethane were sensitive in mixtures with decaborane. Conventional foams were unsatisfactory, largely because explosions at the fuel-foam interface prevented the formation of a coherent barrier. Inert-gas foams produced extinguishment at a reasonable delivery rate; the latter were acceptable at an increased scale of testing, also. A few tests with HEF-3 indicated a lesser degree of suppression difficulty. Young and Eggleston describe the rather indifferent success of other agencies with water fogs, carbon dioxide, and dry chemicals.

The pentaborane manual offered by Olin Mathieson Chemical Co. (Ref. 28) itemizes a long series of materials with which pentaborane is shock sensitive. This list includes numerous halocarbons and "Freons" in general, as well as many oxygen-containing organics. A Callery Chemical Co. brochure (Ref. 29) offers the same information and cites the Olin Mathieson manual as a reference. Neither of these sources provides a bibliography on this subject. Carpenter (Ref. 30) makes note of the violent reactions between halocarbons and boron hydrides and cites a brochure in the Ref. 29 series as his authority. Thus, the experimental work in this area is not referenced, and criteria applied to sensitivity tests cannot be examined to establish the significance of these statements relative to fire suppression. Carpenter mentions the use of water fog and mechanical foam for fire suppression, also.

There may be some danger in overgeneralizing or exaggerating the effect of halide species in association with the boron hydrides. Reaction Motors studied solutions of iodine in pentaborane under contract to The Bureau of Aeronautics.

Control of spontaneous-ignition temperature was achieved, with an optimum
at about 1% (by weight) iodine. Under field conditions, 1% solutions were
reported to ignite only in extreme cases. Solutions containing as much
as 2% iodine were stable, with tests of up to 6-month duration claimed.
An increase in ignition temperature is a useful adjunct to any fire-
suppression technique. Thus, a reappraisal of halogen extinguishants is
indicated. Finally, a recent LPIA survey of HEF fire fighting (Ref. 32)
notes a comment by Callery Chemical Co. on the use of dry chemical
extinguishants. The addition of 5 to 10% potassium or ammonium iodide
is suggested "if the ignition characteristics of HEF-2 are dependent on
chain branching."

In general, candidate fire extinguishants have been selected on the basis
of chain-breaking potential. Reaction with atomic oxygen to give
molecules or a molecule and a maximum of one radical or atom is desired.
The chemicals chosen for consideration in the heterogeneous shock tube
or the diffusion burner, or both, include:

$(CH_3O)_3P$	Br_2 or HBr	(Solution)
PCl_3	I_2 or HI	(Solution)
SF_4	KI	
CCl_4	H_2O	
$(FCl_2C)_2$	NH_3	
$H_3C(CN)$	NaOCN	
$F_3C(CN)$	$(CH_3)_2S$	
$(CH_2CN)_2NH$	$(H_2N)_2CO$	
$HCBr_3$		

In addition, several ultrahigh-surface-area powders were chosen for use
in the shock tube.

The entire preceding discussion is prefaced on the simple problem of fire
suppression; only the capacity of an extinguishant to perform this single

function has been considered. Several possible conditions arise once a
pentaborane fire has been extinguished. Examples are:

1. The residue is subject to detonation or violent decomposition.

2. The residue is stable; unchanged pentaborane remains.

3. Pentaborane persists as a stable, nonvolatile complex.

4. Pentaborane hydrolyzes or oxidizes in the residue, evolving
   hydrogen and boric oxides.

Extinguishment methods and materials leading to condition 1 must be
carefully avoided; this is a situation which creates a hazard that is
equal to or worse than the fire itself. Condition 2 retains the
hazard of volatility with accompanying exposure of personnel to toxic
vapors and possible reignition of combustion. Direct contact with the
residue by personnel is a serious difficulty, also. Conditions 3 and
4 therefore are preferred in practice; however, these may not be equally
applicable to all cases. Note that if a good extinguishant were to
result in condition 2, a second treatment could be applied to achieve
condition 3 or 4.

The chemistry of boron hydrides is treated in Ref. 33 and 34. Pentaborane
hydrolyzes in water rather slowly at normal ambient temperatures. Rapid
hydrolysis is facilitated by the addition of an oxidizing acid.
Destruction is facilitated, also, by reaction with oxygen-containing organics
with a readily replaceable hydrogen (ethanol, dioxane, etc.). Rapid
evolution of hydrogen may be expected to complicate fire suppression. Thus,
pentaborane destruction may be most conveniently carried out as a second
step.

Pentaborane is complexed by Lewis bases; ammonia and organic amines are
common examples of the class of compounds. In many instances these acid-
base complexes are water soluble, stable, and of low volatility. A
residue in the complex form constitutes a minimum hazard; it may be removed
and disposed of "as is" or acidified and hydrolyzed after collection in a

suitable container. The work of Rothberg, Colbourn, and Salvatore (Ref. 35) demonstrates the reduction of personnel contact hazards by complexing treatment. Various aqueous detergent and solvent solutions were evaluated as decontaminants in animal experiments. A 2.8% solution of ammonia in water was appreciably better than the other solutions of non-Lewis bases. It resulted in 100% specimen recoveries, even after a 15-minute delay between exposure to four times the LD_{50} of HEF-3 and decontamination. One of the objectives of this program is the evaluation of various compounds, in aqueous solution, as means of complexing or destroying pentaborane quantitatively.

DIFFUSION FLAME STUDIES

APPARATUS AND PROCEDURES

The choice of a diffusion flame experiment, as opposed to a premix flame
or the gas-phase explosion burette, was prefaced on three considerations.
First, practical fires are usually heterogeneous diffusion flames; they
propagate by means of (1) heat and mass transport processes in the region
between the flame and the liquid fuel and (2) oxygen diffusion to the
flame through convecting combustion products. Under normal circumstances,
a volatile fire extinguishant such as carbon tetrachloride will vaporize
and diffuse to the flame much as oxygen does. An effort was made to select
an experiment that would incorporate as many of the features of a field
situation as possible. Second, flame speeds of boron hydrides in air are
quite large. In air, at an equivalence ratio of 1.2, pentaborane has a
flame speed of almost 600 cm/sec. This is over twice the maximum flame
speed for hydrogen in air. Berl et al. (Ref. 26) note that a conventional
laminar premix flame would require a "burner tube of 1-millimeter diameter
or less to prevent flashback while maintaining laminar flow." Alternate
methods of studying fast premix flames, such as explosive soap bubbles, are
so complex as to appear impractical for the investigation of suppressants.
Diffusion flames are free of flashback difficulties. Finally, one of the
pentaborane combustion products is condensable to a solid. There was much
concern over the possible deposition of boric oxide on a burner tip or
burette walls, with accompanying flow disturbances, flowrate variations,
and/or changes in wall characteristics. Lifted diffusion flames, i.e.,
flames detached from the burner tip, have been observed by numerous
workers (Ref. 36). The laminar jet burner reported by Potter et al.
(Ref. 37) is another form of diffusion flame which yields a detached
flame. Diffusion flames therefore provide an opportunity to bypass the
problem of solid formation and deposition by permitting detachment of
the flame zone from apparatus surfaces.

Diffusion flames can be classified on the basis of the flow pattern of
fuel and oxidizer streams. Fuel and oxidizer flows can be counter-
current or parallel, or fuel can pass through stagnant oxidizer. Further
subclassification is related to a turbulence index; thus the terms
laminar and turbulent are applied as a function of Reynolds number or
shadow photographic evidence. Either of these criteria may be applied
to the combustion zone or combustion product flow, while the former may
be applied to tube flow of fuel and oxidizer feed streams. The jet
burner is an example of a countercurrent-flow flame device. Concentric
annulus and slit burners are examples of the parallel-flow type; simple
fuel jets and candle flames are of the stagnant-oxidizer type.

Friedman and Levy (Ref. 11) screened a series of covalent halide in-
hibitors with a laminar jet flame of methane and air. They describe
a method of comparison which relies upon the visible structure of the
flame. Initially, this flame is the shape of a rounded disk normal to
the reactant streams. As flowrates are increased or as inhibitors are
added, a hole develops at the center of the disk and the flame takes on
a toroidal form. The appearance of the hole, as a function of fuel
flow and inhibitor concentration, is the criterion for inhibitor evalua-
tion. The flame must be shielded, and Friedman and Levy encountered
difficulty with solid deposition during experiments with alkali-metal
addition. Further, the subjective nature of this evaluation and the
high intensity of pentaborane flames led to rejection of the jet burner
for this program.

It was desired to introduce suppressants, in the vapor phase, by means
of the oxidizer feed to the burner. This procedure eliminated any prob-
lems of compatibility between pentaborane and the individual suppressant
candidates. In addition, inhibiting effects are enhanced by introducing
suppressants with the oxidizer feed. Friedman and Levy (Ref. 1) report
that a premix methane-air flame is extinguished by 4.8% methyl bromide.
Only 3.8% methyl bromide was required to extinguish a diffusion flame
when introduced into the air stream; however, the same diffusion flame
required 47% of the additive when it was introduced in the methane. The
operation of a simple fuel jet burner was rejected, also.

The choice between concentric-tube and slit-type, parallel-flow burners
was made on a purely practical basis. As a minimum, some boric oxide
deposition was expected during startup and shutdown, and removal had
to be anticipated. The concentric-tube design appeared to be more
amenable to frequent cleaning; for this reason, it was selected. Initial
design of the burner provided for fully laminar flow in the tubes at the
burner exit. Equal fuel and oxidizer velocities of about 10 ft/sec and
Reynolds numbers in the range of 1500 to 2000 were planned. It will
be seen that a lifted flame was not attainable under these conditions,
and final operation of the burner was carried out with turbulent inlet
conditions for both streams.

The burner consisted of a 1/8-inch, stainless-steel tube inside a piece
of 1-inch, stainless-steel tubing. The inner tube was held in place
with positioning pins to ensure concentricity; the exit ends of the
two tubes were cut off in the same plane. An adapter piece was pressed
into the outer tube to achieve the required annulus dimension and cal-
culated air-flow channel. Final annulus dimensions were 0.500-inch outer
diameter and 0.125-inch inner diameter; fuel tube inner diameter was
0.101 inch.

Figure 1 is a schematic diagram of the diffusion flame system in final
form. Pentaborane vapor was prepared in a 2-quart, stainless-steel
tank. Pressure was monitored with a 0 to 30-psia Statham pressure trans-
ducer; transducer output was recorded and, also, employed to operate a
limit switch and relay in the tank heater power supply. Pressure was
maintained within +0.05 psi of the set point. Pressure was selected
as the boiler control variable because of the appreciable temperature
gradients in the tank arising as a consequence of the absence of agitation.
Relating pressure to vapor temperature with the vapor pressure data for
pentaborane gave estimated temperature control limits of ±0.2 F.

Prepurified nitrogen was employed as a purge and carrier gas for the
pentaborane. This material has a guaranteed purity of 99.996% and a
maximum oxygen concentration of 8 ppm. Nitrogen pressure, temperature
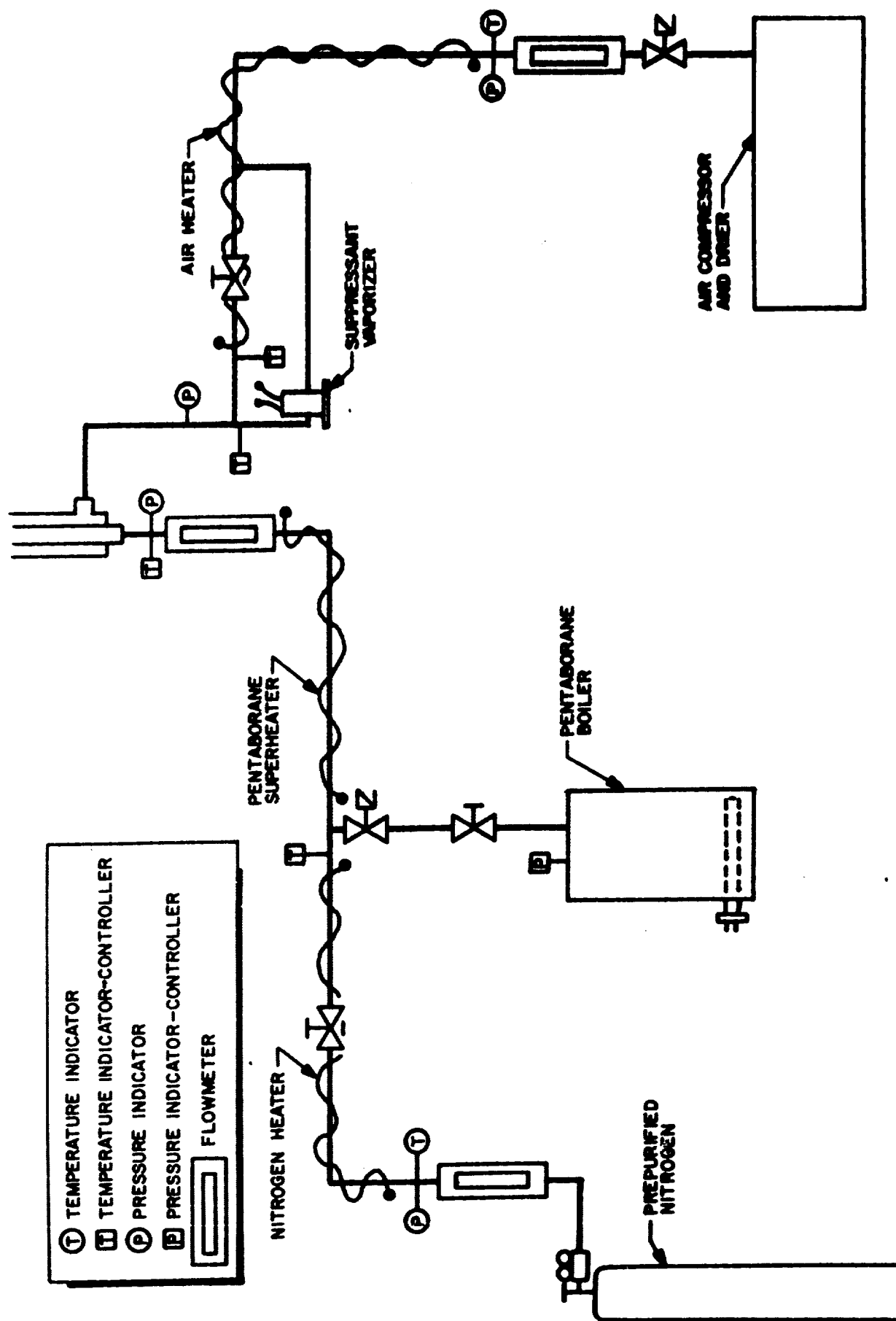
Figure 1. Schematic of Diffusion Flame System

Legend:
- (T) TEMPERATURE INDICATOR
- [T] TEMPERATURE INDICATOR-CONTROLLER
- (P) PRESSURE INDICATOR
- [P] PRESSURE INDICATOR-CONTROLLER
- FLOWMETER

AIR HEATER

SUPPRESSANT VAPORIZER

AIR COMPRESSOR AND DRIER

PENTABORANE SUPERHEATER

PENTABORANE BOILER

NITROGEN HEATER

PREPURIFIED NITROGEN

and flowrate were measured just downstream of the bottle regulator.
Nitrogen was heated to about 130 F prior to reaching the nitrogen-
pentaborane mixing tee. Temperature was maintained within ±3 F with
a Wheelco indicator/controller. Mixture temperature was maintained
with a similar device. Pentaborane vapor and pentaborane-nitrogen
mixtures were superheated enough to prevent condensation in the fuel feed
lines. Temperature, pressure, and flowrate were measured immediately
upstream of the burner inlet. For the greater part of the program,
mixture feed temperature was controlled at 145 ±2 F.

Flame air was supplied with a commercial compressor/drier set. In turn,
air was heated to about 240 F; a Wheelco indicator/controller was
employed to maintain constant temperature. Initially, suppressants
were introduced from a boiler of the same design as the pentaborane
boiler. However, because of the corrosive nature and wide range of
boiling points of most candidate suppressants, this system did not
function properly. Further, excessive time was required to change
suppressants and to carry out the necessary tank heating and cooling
cycles. An alternate scheme was put into service.

A heated inlet from a preparative-scale gas chromatograph was placed in
a bypass in the heated-air line. This device consisted of a large
piece of metal, in the form of a hollow cylinder, that was wound with
heating wire and could be raised to very high temperatures. A tempera-
ture sensor was placed in the air stream below the vaporizer and connected
to an indicator/controller system based on a Leeds and Northrup strip
recorder. Air stream temperatures of 450 ±10 F were maintained at
the exit of this heated-inlet system. Quantities of liquid suppressant
were injected into the vaporizer through a rubber septum from standard
laboratory syringes. As much as 2 cubic centimeters (cc) of liquid
could be vaporized within 1 second.

Burner operation was begun by starting nitrogen and air streams and
bringing all lines to desired temperatures. The pentaborane boiler
was heated and allowed to come to set-point pressure, i.e., about 5 psig.
The suppressant vaporizer was brought to operating temperature, also.

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Once control was established, the shutoff and needle valves on the
pentaborane boiler were opened slowly, and pentaborane vapor was intro-
duced to the burner. A Testla coil was employed for ignition. Penta-
borane flow was increased and nitrogen flow was decreased until the
desired concentration and flowrate were attained. The pressure ratio
across the valve between the nitrogen supply and the pentaborane mixing
tee was kept high, i.e., in excess of 2.5, to ensure sonic flow. Thus,
disturbances in the pentaborane feed did not disturb nitrogen flow; i.e.,
the latter remained a relative maximum due to choking.

The procedure for suppressant evaluation consisted of the NOL up-and-
down technique, as frequently applied to sensitivity testing. The
criterion of a positive result was complete extinguishment of the flame
within a period of 2 to 3 seconds. Disturbances and suppressant flames
were discounted as negative results. Three separate levels of suppressant
addition were used to gain increased sensitivity. Quantities of 0 to
0.2 cc were injected with a 0.2-cc syringe at increments of 0.01 cc.
Quantities of 0.2 to 0.7 cc were injected with a 1-cc syringe at
increments of 0.05 cc and, in the upper range, quantities of 0.7 to 2.0
cc were injected with a 2-cc syringe at increments of 0.1 cc.

In each series of tests, a steady flame was attained and an approximate
level of suppressant addition for total extinction was established by
three to six preliminary injections. Starting from this estimated ex-
tinction point, quantities of suppressant were varied by one range in-
crement until a reversal of trend was note; i.e., if the preceding
quantity injected failed to extinguish the flame, a quantity larger by
one range increment was injected. If a preceding quantity successfully
extinguished the flame, the subsequent test employed a quantity smaller
by one range increment. Injections were continued until the mean volume
of liquid necessary to extinguish the flame with a 50% probability could
be estimated accurately. The number of tests in a given series varied
from 25 to 50. Results were tabulated as 50% suppressant addition level
vs pentaborane concentration.

In some instances, a change from all positive to all negative results took place over one range increment. The midpoint of the increment was taken as the 50% suppressant level. When a broader range of variation was observed, the sample was assumed to be normally distributed. The fraction of positive observations was plotted against suppressant level on Gaussian probability paper. The 50% level was taken from the best straightline fit to the data.

RESULTS

Preliminary burner experiments were carried out with simple jet and parallel-flow flames of methane, methanol, and hexane with air. Results were reproducible and qualitatively consistent with the observations for hydrocarbon diffusion flames reported by Hottel and Hawthorne (Ref. 38) and Wohl, Gazley, and Kapp (Ref. 39). Controls performed well and measurements were repeatable. The phenomenon of liftoff was observed and easily controlled in all three cases. The next step in the program was to introduce pentaborane and establish a region of composition and flow velocities for liftoff.

Under no circumstances was a pure pentaborane flame observed to lift off the burner tip. As had been expected, the deposition of boric oxide on the burner tip at the fuel port proved to be a serious problem. Flowrate and flame properties could not be maintained within reasonable limits and, to hold a flame, continuous manual scraping of the burner tip was required. Dilution of the pentaborane stream with prepurified nitrogen was used to detach the flame and provide steady operating conditions.

Well behaved, lifted-off pentaborane flames were observed at nitrogen flowrates of 450 to 850 cu in./min referred to 14.7 psia and 32 F (scim). Allowable pentaborane concentration varied with nitrogen flowrate; over-all limits were 10 to 30% fuel. Best results were achieved with a

slight increase in air flow beyond that planned in the design. Final air-flow conditions were:

1. Temperature, F   240
2. Tube exit velocity, ft/sec   12.1
3. Reynolds number   2350

Final fuel stream conditions were chosen on the basis of (1) a broad range of pentaborane concentrations at fixed nitrogen flow and (2) ease of control. Nitrogen flowrate was 660 ±10 scim. Pentaborane concentration was variable from 14 to 27% without flame attachment. Below 14% the flame was unstable, and above 27% it attached itself to the fuel tube exit. Fuel flow conditions were:

1. Temperature, F   145
2. Tube exit velocity, ft/sec   164 to 188
3. Reynolds number   6500 to 7500

Note that both oxidizer and fuel streams were in turbulent tube flow at the feed tube exits, with the fuel stream well into the turbulent regime. Also, fuel stream velocities were 13 to 15 times greater than the air velocities under these conditions. Figure 2 is a photograph of a lifted flame with a pentaborane concentration of 16% at a nitrogen flowrate of 660 scim.

A full summary of all suppressants tested and detailed results appear in Tables 1 through 4. The nature of the results makes it simplest to classify and discuss the results on the basis of elemental substituents. Halides, nitrogen, sulfur, and phosphorus are the distinguishing elemental types. The results of up-and-down extinction level tests are presented graphically in Fig. 3 through 5. Halogen compounds are grouped in Fig. 3, nitrogen compounds and their aqueous solutions are grouped in Fig. 4, and both sulfur and phosphorus compounds are presented in Fig. 5. Water is included as a reference on all these figures.
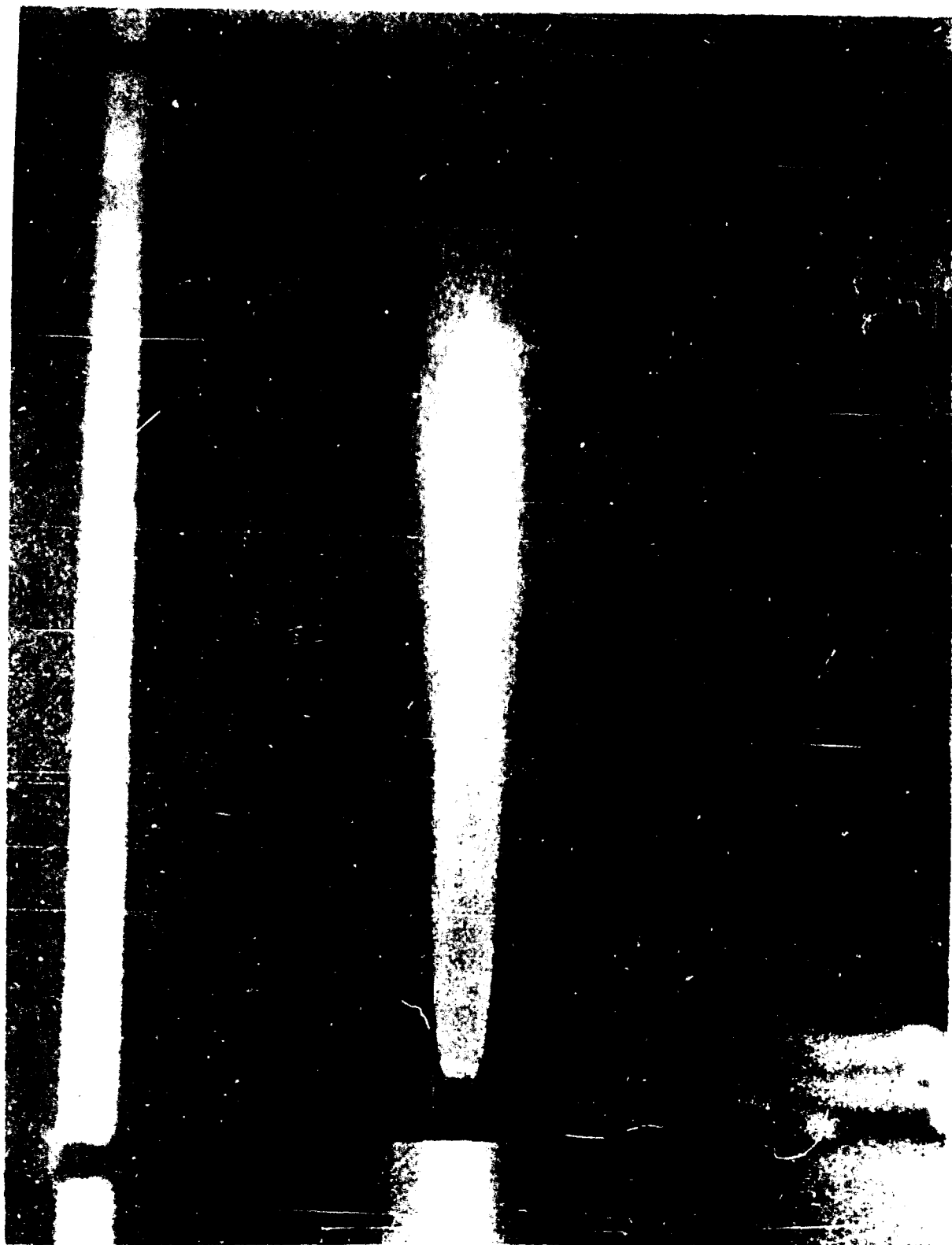
Figure 2. Detached Flame of Pentaborane-Nitrogen in Air
(Reference dimension: burner tip is 1-inch
diameter)

TABLE 1

DIFFUSION FLAME EXTINCTION
(HALOGEN SUPPRESSANTS)

Suppressant	Nitrogen Flow, scim	Pentaborane Concentration, volume percent	Total Fuel Flow, scim	Fifty-percent Suppressant Level, cc
Carbon Tetrachloride	665	14.8	780	0.26
	660	17.6	800	0.58
	660	20.2	830	0.88
	660	22.3	850	~1.72
Freon TF	655	16.3	785	0.27
	660	17.2	800	0.18
	660	18.6	810	0.98
	665	18.7	815	0.98
	Increased flame intensity at higher pentaborane concentrations			
Bromoform	660	18.6	815	0.65
Trichloro-ethylene	660	19.8	820	~1.00
Dichloro-methane	660	20.2	825	0.48
Carbon Tetrachloride +2% Iodine	660	20.3	825	0.55
Sulfur Tetrafluoride	Increased flame intensity at all pentaborane concentrations			
Methyl Iodide	660	20.0	820	0.14
	660	22.7	850	0.18
	660	25.0	880	0.27
	660	26.5	895	0.32

TABLE 2

DIFFUSION FLAME EXTINCTION
(NITROGEN SUPPRESSANTS)

Suppressant	Nitrogen Flow, scim	Pentaborane Concentration, volume percent	Total Fuel Flow, scim	Fifty-percent Suppressant Level, cc
Water (Ref.)	660	16.6	79C	0.23
	660	19.2	815	0.38
	660	20.1	830	0.54
	665	22.4	855	0.68
Increased flame intensity at all higher pentaborane concentrations				
Acetonitrile	660	15.2	780	0.26
	660	19.0	815	0.38
	655	21.4	830	0.52
	660	22.3	850	0.56
Attained flammability limit of acetonitrile in air				
20% Aceto-nitrile + Water	660	15.8	780	0.17
	655	18.1	800	0.25
	665	19.7	825	0.25
	660	22.8	855	0.74
28 to 30% Ammonia + Water	660	15.0	775	0.095
	660	17.4	800	0.155
	665	19.7	825	0.175
	660	22.9	855	0.65
Increased flame intensity at all higher pentaborane concentrations				
9 to 10% Ammonia + Water	665	15.5	785	0.17
	665	17.5	805	0.63
No inhibition at higher pentaborane concentrations				
Ethylene-diamine	665	19.9	825	0.45
Pyridine	Burned readily in air, no inhibition			
Propionitrile	Burned readily in air, no inhibition			
β,β'-Oxydi-propionitrile	No inhibition			

TABLE 3

DIFFUSION FLAME EXTINCTION

(SULFUR SUPPRESSANTS)

Suppressant	Nitrogen Flow, scim	Pentaborane Concentration, volume percent	Total Fuel Flow, scim	Fifty-percent Suppressant Level, cc
Dimethyl Sulfide	660	15.0	780	0.055
	660	17.6	800	0.075
	660	17.7	805	~0.9
	Attained flammability limit for dimethyl sulfide in air			
Diethyl Sulfide	Burned readily in air, no inhibition			
Thiophene	Burned readily in air, no inhibition			
2-Bromo-thiophene	No inhibition			
Carbon Disulfide	Burned readily in air, no inhibition			
Perchloro-methyl-mercaptan	665	16.4	795	0.95
Benzene Sulfonyl chloride	No inhibition			

TABLE 4

DIFFUSION FLAME EXTINCTION

(PHOSPHORUS SUPPRESSANTS)

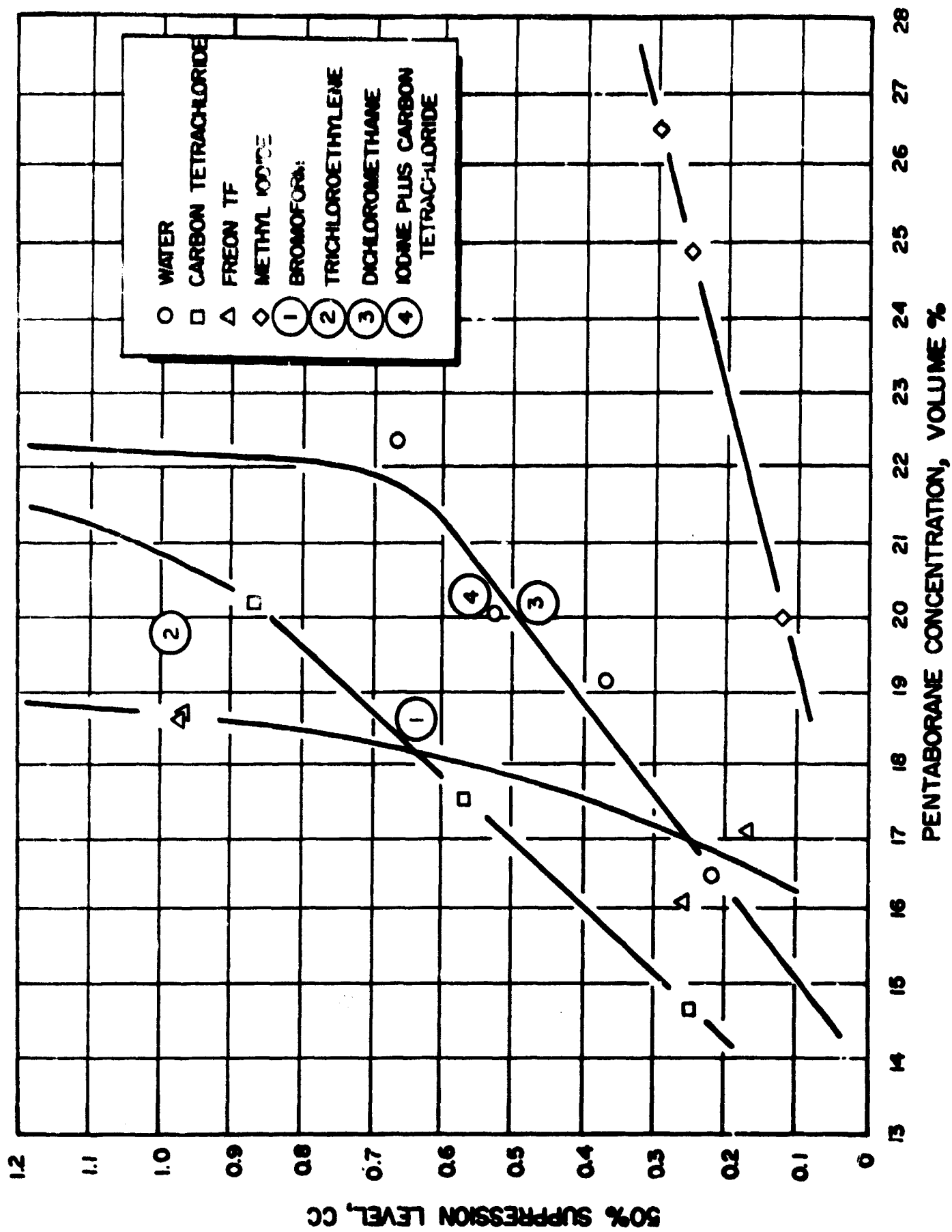| Suppressant	Nitrogen Flow, scim	Pentaborane Concentration, volume percent	Total Fuel Flow, scim	Fifty-percent Suppressant Level, cc
Trimethoxy-phosphine	660	16.7	785	0.45
	660	17.8	805	0.40
	660	19.4	820	1.33
Triethoxy-phosphine	660	18.2	805	0.55
Dimethyl Hydrogen Phosphite	No inhibition			

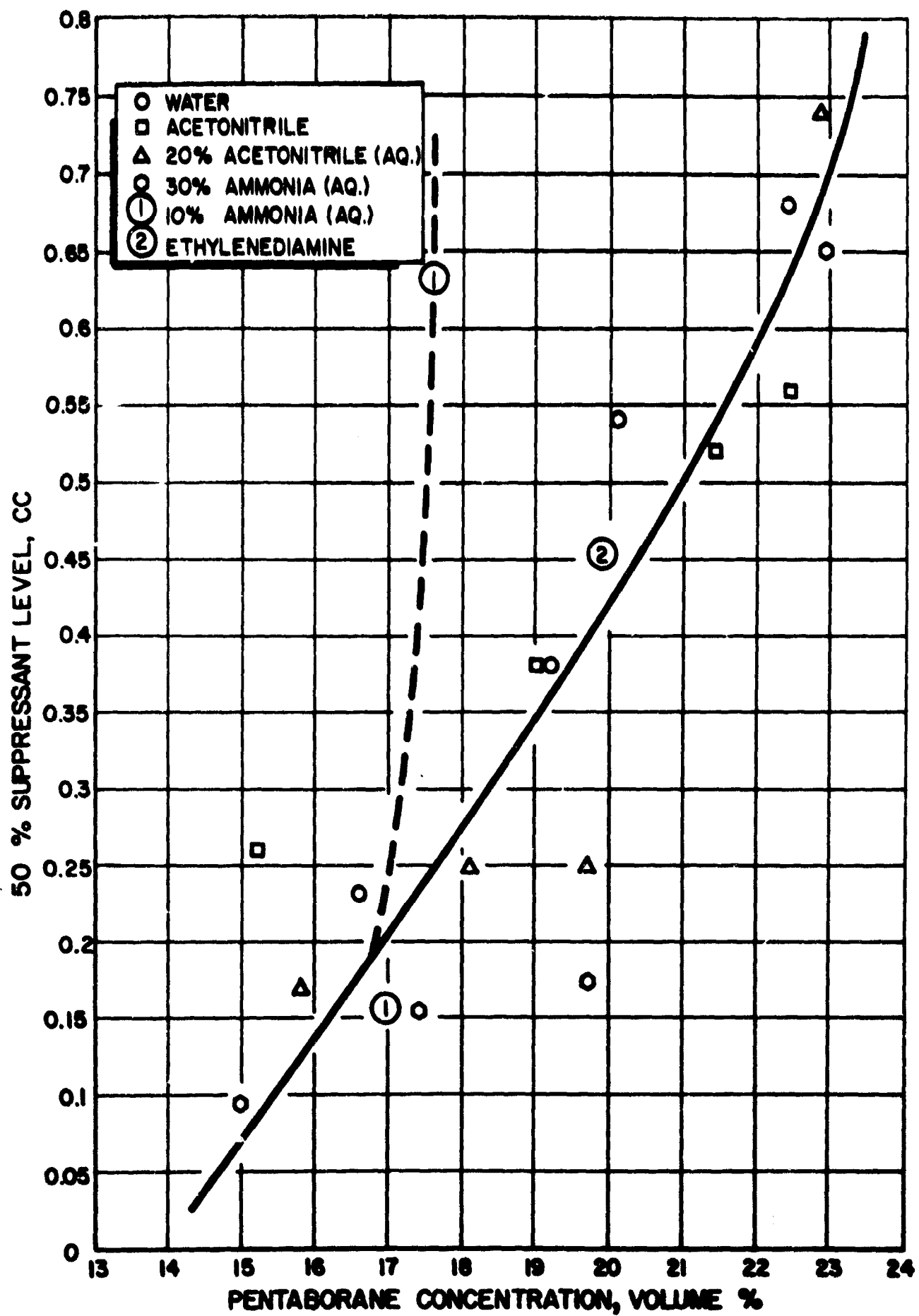Figure 3. Suppressant Efficiency of Halogen Compounds

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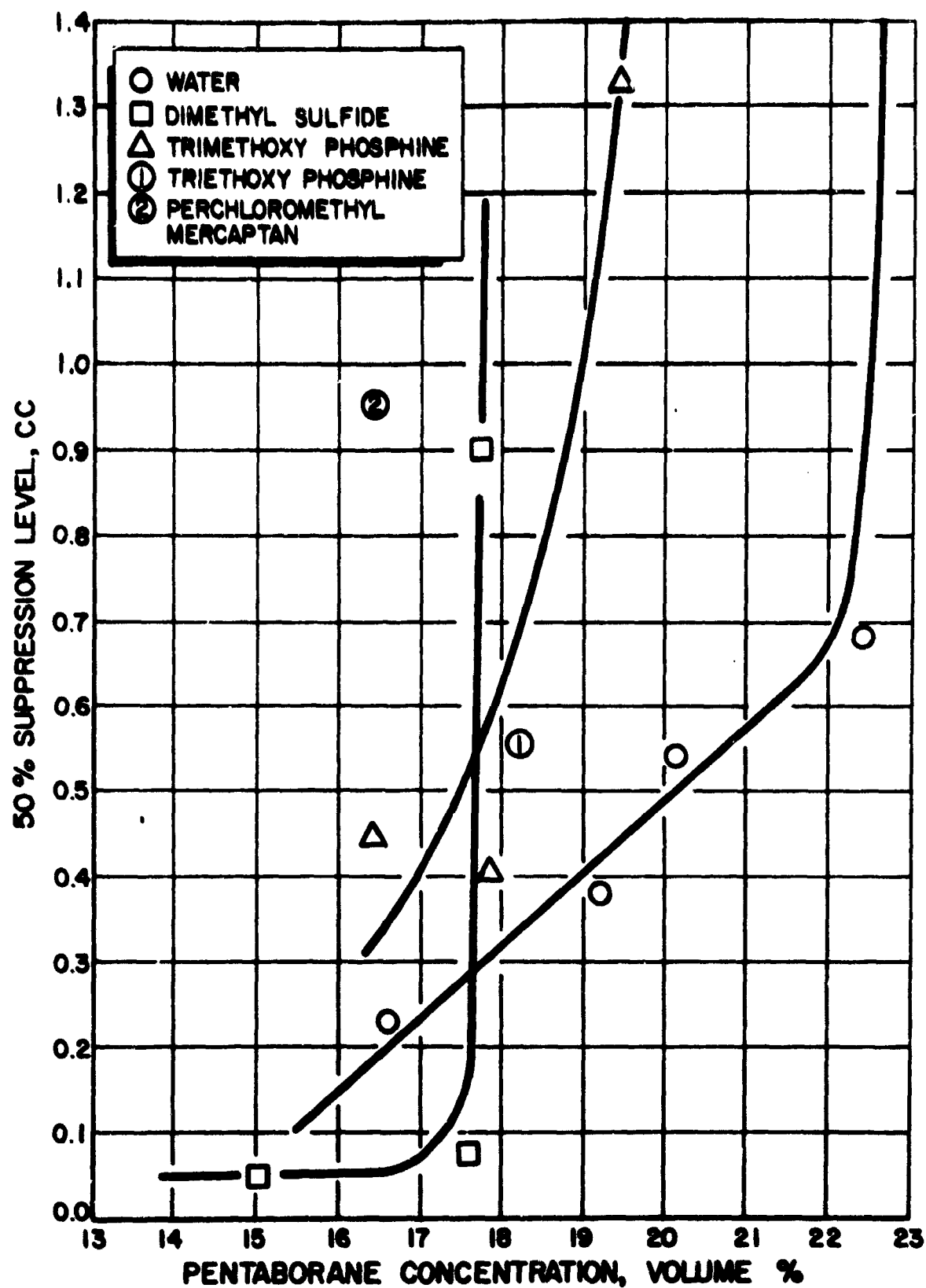Figure 4. Suppressant Efficiency of Nitrogen Compounds

Figure 5. Suppressant Efficiency of Sulfur and Phosphorus Compounds

Figure 6 is a pair of typical distribution diagrams for water and trichloro-trifluorethane (Freon TF). At the lower suppressant levels (e.g., water in Fig. 6a), nearly all changes from positive to negative took place over one range increment. At the higher suppressant levels (e.g., Freon TF in Fig.6b), changes in trend occurred over two or three range increments. In the aggregate, transition regions amounted to 25% of the 50% suppressant level, i.e., the mean suppressant addition plus or minus 12.5 percent. Thus, the relative scatter did not appear to vary significantly with suppressant level.

The 50% suppressant level for water increased approximately linearly with pentaborane concentration to 22% pentaborane in the fuel stream. At the latter condition, water was no longer able to extinguish the fire; only some spurious positive results were obtained at levels exceeding 2.0 cc. Water appeared to intensify these fuel-rich flames. Carbon tetrachloride increased linearly, also, although at a higher suppressant level; it broke sharply at about 22%, just as the water, and appeared to intensify the flame at the higher fuel concentration. Sulfur tetrafluoride had no inhibiting effect; it intensified the flame at all concentrationsof pentaborane and at all levels of addition. Freon TF had some inhibiting effect but broke at a low fuel concentration. Single experiments with bromoform and trichloroethylene were comparable with the results for carbon tetrachloride, while single experiments with dichloromethane and 2% iodine in carbon tetrachloride compared best with water data.

Methyl iodide was significantly superior to water. The mean volume of suppressant required for flame extinction was less. Further, suppressant effects persisted to the upper concentration limit of a detached flame (about 26.5%). Both water and carbon tetrachloride intensified the penta-borane flame at fuel concentration in excess of about 22.5%. Thus, methyl iodide exhibited good volumetric efficiency and an extended range as well.

```
0.30    +                              +

0.25       +   +   +   +   +   +   o   +   +   +
                                              ─────── 0.23
0.20    o    o   o   o   o   o          o   o
```
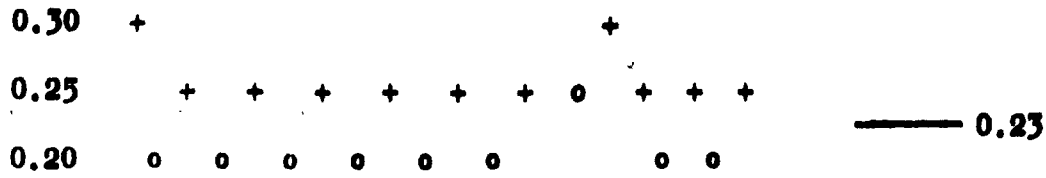
Figure 6a.   Distribution Diagram for Water

```
1.2

1.1    +              +                    +    +

1.0    o +   +      o   +        +        +  o   o   +   o───── 0.98

0.9    o    o    +  o       +  o   o          o          o

0.8               o           o
```

Figure 6b.   Distribution Diagram for Freon TF

Acetonitrile did not differ from water with respect to mean suppressant level or range of action. At the upper limit of suppression, water intensified the flame. Under the same conditions, the volume of acetonitrile required for extinction exceeded its flammability limit based on annular air flow. The green color that is typical of boron hydride combustion was weakened and replaced by an annular orange-purple flame of acetonitrile. As the suppressant concentration diminished, the pentaborane flame reappeared spontaneously.

Aqueous acetonitrile (20%) and aqueous ammonia (30%) were not significantly different from water or acetonitrile. At lower fuel concentrations, negative deviations from the general trend were observed; however, the upper limit of suppressant action remained unchanged. Both solutions intensified the flame at 22.5% pentaborane. The data point for 10% aqueous ammonia followed another pattern. A point of flame intensification was reached at a pentaborane concentration of less than 18%. The results shown in Fig. 4 were accompanied by an experiment with an 18% flame that could not be extinguished with over 2 cc of solution. Finally, ethylenediamine gave a point that fell within the probable limit of the general curv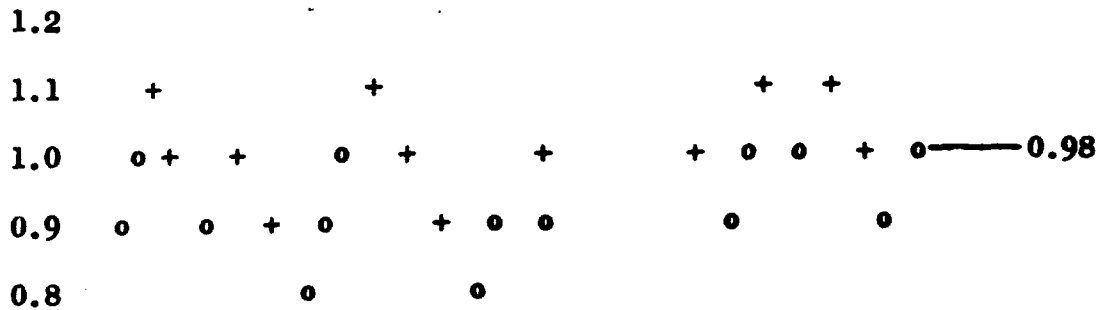e. Pyridine and propionitrile burned readily in the annular air and had no inhibiting effect on the pentaborane flame. β, β'-oxydipropionitrile did not burn and did not affect the flame in any way.

At low pentaborane concentrations, dimethyl sulfide is the most efficient of all suppressants tested. However, it reached a flammability in the carrier air at a fuel concentration of less than 18%. Diethyl sulfide, carbon disulfide, and thiophene burned readily with the annular air and exhibited no flame inhibition. Benzene sulfonylchloride and 2-bromothiophene had no effect on the flame; this appeared to be due to low volatility and reduced vaporization rate from the heated inlet. Perchloromethyl mercaptan showed poor efficiency in one test with a weak flame.

Trimethoxyphosphine was appreciably less efficient than water. Tri-
ethoxyphosphine gave one point that was consistent with the data for
its methyl homolog. Dimethyl hydrogen phosphite had no effect; this
was attributed to low volatility (as in the case of the sulfur compounds
noted above).

DISCUSSION

The presence of fluorine in a suppressant is undesirable. Both Freon
TF and sulfur tetrafluoride augmented the pentaborane diffusion flame by
acting as supplementary oxidizers. Although the former exhibited good
volumetric suppression efficiency at low pentaborane concentrations, it
passed through a transition at a very low fuel flow and contributed
markedly to the flame. Flame color comparisons indicated that sulfur
tetrafluoride reacted with pentaborane under all conditions.

Carbon tetrachloride performed less efficiently than water. Both ceased
to inhibit the diffusion flame at about the same pentaborane concentration;
at leaner fuel levels, smaller volumes of water were required for extinc-
tion. Trichloroethylene was run to test the significance of a carbon-
to-carbon linkage in the suppressant molecule. It was thought that this
factor might have influenced the behavior of Freon TF. However,
trichlorethylene gave a point within the probable limits of the carbon
tetrachloride data. Conversely, a data point for dichloromethane fell
on the water curve; i.e., it was well below the carbon tetrachloride
curve. In the case of hydrocarbon fires, the efficiency of chloromethanes
is directly related to the number of chlorine atoms. The superiority of
dichloromethane suggested that this rule does not directly apply to
pentaborane fires.

In general, the suppression effect of halides on hydrocarbon fires is
enhanced with increasing atomic number. Organic bromides and mixed
halo-compounds containing bromine are good hydrocarbon fire extinguishants.
A test with bromoform, however, had about the same result as carbon
tetrachloride on a pentaborane flame. Thus, the presence of three bromine

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atoms per suppressant molecule did not yield any measurable improvement in performance. Iodine is the best of the halides with respect to hydrocarbon combustion, and, unlike the bromine effect, this pattern also appears in the case of pentaborane. As little as 2% iodine in carbon tetrachloride yielded a point that fell on the water curve. This is a major improvement in efficiency. Finally, methyl iodide is by far the best of the additives tested. It has an excellent volumetric efficiency, i.e., low 50% suppressant level. Further, it extinguished the entire range of detached flames. There was no abrupt change to a more intense flame that was characteristic of other moderately good suppressants.

The effect of iodine can be related to the halogenation reactions of boron hydrides. All of the latter react violently with fluorine, while most react rapidly with chlorine. Reactivity decreases with increasing molecular weight of the hydride and increasing atomic number of the halide. Thus, decaborane does not react spontaneously with chlorine at room temperature. Bromine and iodine reactions are slower and lead to stable intermediate species. The iodide of diborane, B_2H_5I, is stable and not spontaneously reactive in air; the iodide of pentaborane is stable and unreactive as well.

Elemental iodine and methyl iodide dissociate readily at elevated temperatures to yield iodine atoms and methyl radicals in the latter case. Reaction of methyl radicals is relatively slow, while it is probable that the suppression action of iodine is associated with the formation of relatively unreactive halide intermediates by reactions between hydride radicals and iodine atoms. The higher reactivity of fluorine and chlorine are consistent with the absence of effective inhibition by organic compounds of these halides. The poor showing of bromoform cannot be explained on the basis of the proposed inhibition scheme; however, the evaluation of other organic bromides may lead to a suitable explanation.

Reaction with hydride radicals is one of the approaches to chain breaking that was noted in the general discussion. The effects of iodine are clear evidence of a chain-branching mechanism and confirm the validity

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of a purely chemical approach to flame inhibition. Initially, more
success in dealing with oxygen atoms to prevent branching had been antici-
pated; however, the data for halide additives are most easily explained
by the alternate process of reaction with hydride radicals.

The observations of iodine performance in the diffusion burner are
compatible with the effect of iodine on the ignition properties of
pentaborane when it is present as a solute in the latter. Iodine atoms
can be expected to inhibit the branching process that probably underlies
pentaborane ignition. In contrast, explosion burette test results pre-
sented later showed that an aqueous solution of potassium iodide and
iodine amplified rather than suppressed a heterogeneous pentaborane-air
detonation. The observation that water augments a pentaborane diffusion
flame under some circumstances can be drawn upon. Since water is the
more volatile species in a solution of iodine in aqueous potassium iodide,
the stimulation of a responsive reaction is a probable consequence of
the presence of water vapor in the shock tube environment. Shock tube
tests of water as a liquid suppressant and tests with a solution of
iodine in pentaborane would help to clarify this issue.

Various amines and nitriles were tried as vehicles for oxygen atom-
trapping reactions. Acetonitrile was very much like water in terms of
volumetric efficiency. However, at the upper limit of suppression it
reached a definite flammability limit without the flame augmentation
of water. The equivalence of the limiting pentaborane concentration
is highly coincidental. Ethylenediamine compared with acetonitrile.
Aqueous solutions of ammonia and acetonitrile both augmented the flame
at their upper suppression limits; i.e., they behaved like water. A
20% solution of acetonitrile and 30% solution of aqueous ammonia exhibit
the same suppression limit as plain water. Conversely, a 10% solution
of ammonia produced an intensified flame at a very reduced fuel
concentration. Finally, several nitriles and amines burned readily and
exhibited no inhibiting effect whatever.

These results gave little promise of effective suppression of penta-
borane combustion by reacting chain-carrying oxygen compounds with
nitriles, amines, or their aqueous solutions. As the additive concen-
tration increases to a useful level, the organics enter into secondary
combustion, and there is a simple superposition of competing oxidation
reactions. The aqueous solutions tested generally augment the penta-
borane flame in the same way as pure water. Trapping oxygen atoms in this
way appears to be of doubtful value.

Trimethyl and triethyl phosphites were investigated as oxygen atom traps,
also. Both showed very poor efficiency in performing this function; they
were less efficient suppressants than water. The possible utility of
reactions with oxygen atoms, however, was successfully demonstrated with
dimethyl sulfide. This compound exhibited the highest volumetric
efficiencies of any tested. Diffusion flames of up to 17.5% pentaborane
in the fuel were suppressed by as little as 0.05-cc dimethyl sulfide.
At this fuel concentration, the quantity of suppressant required
corresponded to the flammability limit in the annular air. Thus, the
practical value of dimethyl sulfide is limited. Nonetheless, the results
gave added support to a chain-branching mechanism for pentaborane oxida-
tion and verified the concept of inihibition by means of trapping the
oxygen atoms that act as a chain carrier. Several other sulfur compounds
burned even more readily and exhibited no suppressant qualities. The over-
all results of the diffusion burner studies have extended the evidence
for a chain-branching mechanism. Further, the combined evidence
supplied by dimethyl sulfide and methyl iodide strongly suggest that
chemical inhibition can be achieved by trapping either the hydride
radical or oxygen atom chain carrier species.

EXPLOSION BURETTE

APPARATUS AND PROCEDURES

The "explosion burette" has been employed by the Bureau of Mines and
others to obtain a variety of data on combustion processes. Measure-
ments include flame speed, detonation velocity, and flammability limits.
In general, this apparatus has been employed on gaseous mixtures of fuel
and oxidizer. Once detonation has begun, there is little to distinguish
this device from a conventional shock tube. In fact, the only real dif-
ferences are (1) the method of initiation and (2) application of the
former to phenomena occurring at less than the speed of sound.

The purpose in selecting an experimental technique other than the dif-
fusion burner was to find a convenient way of evaluating the effects of
candidate additives, dispersed as a solid or liquid phase, on the sup-
pression of combustion of fine-particle sprays of pentaborane in air.
An instrumented tube or burette was chosen as the basic apparatus;
heterogeneous mixtures were to be prepared by injection of fuel into
still air within the tube. The success of Webber (Ref. 40) and Cramer
(Ref. 41) in shock ignition of heterogeneous hydrocarbon-air mixture
prompted the selection of a shock tube technique of operation, i.e.,
preparation of the combustion system in the tube and ignition with the
shock from a hydrogen-oxygen mixture burned in a short "driver" section.

Webber introduced kerosene into pure oxygen; in some cases, the sprays
were ignited with a pyrotechnic igniter prior to pulsing. He concluded
that the pyrotechnic device was not required; a coarse spray of non-
volatile fuel could be ignited directly by the pressure wave. Further,
the fuel was vaporized and burned rapidly enough to amplify the pulse
as it passed through the droplet field. Prevaporization or partial com-
bustion was not necessary. Cramer extended this work and showed that
pressure amplification occurred reproducibly only at oxidation ratios,
i.e., actual oxidizer to stoichiometric oxidizer weight ratio of 0.27
to 0.55. Near stoichiometric no amplification was observed. He found
that pressure ratios and shock velocities in a heterogeneous field are

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close to the theoretical for the gas phase alone. Cramer postulates that droplets are shattered mechanically and burn rapidly in the high-pressure, high-temperature postshock regime.

The pentaborane shock tube consisted of a single length of 2-inch, schedule 40, stainless-steel pipe; actual length was 62-1/4 inches. One end was flanged to accept the driver section and a port for the injection of solid explosion suppressants. Six ports for Photocon, type 525 pressure transducers were located along the tube at intervals to facilitate monitoring the progress and strength of any pressure pulse. The first port was located 3 inches from the driver section flange; subsequent ports were spaced at 12-inch intervals. Transducer ports were designed so that the diaphragm of a mounted transducer was flush with the inner wall of the shock tube.

Pentaborane was introduced from three injectors located at distance of 6, 30, and 54 inches from the driver section flange. Sprays from the first and last injectors were directed inward; the spray from the center injector, which had twice the capacity of the outer injectors, was split and injected in both directions. Two injectors, identical to the central pentaborane injector, were employed for liquid explosion suppressants. The suppressant injectors were located at distances of 18 and 42 inches from the driver section flange; sprays were injected in both directions from each. Figure 7 is a schematic of the shock tube arrangement; Fig. 8 is a photograph of the installation.

Figure 9 is a drawing of the injectors. The probe was 1/8-inch OD tubing and the injection ports were No. 80 drill (0.0135-inch diameter) holes located on the centerline of the tubing. Alignment pins were provided to ensure that the injection ports were always oriented parallel to the axis of the shock tube. All injectors had a check valve arrangement; they could be loaded with pentaborane in a glove box and transferred to the shock tube without leakage or oxidation of the fuel. A threaded stop was used to control the ullage of the injector; it could be preset to the amount of fuel or suppressant required for any particular test. The signal to inject was followed by solenoid valve

DRIVER
SECTION

P

PENTABORANE INJECTOR

S

SUPPRESSANT INJECTOR

PHOTOCON TRANSDUCER
(* INDICATES POSITIONS USED)
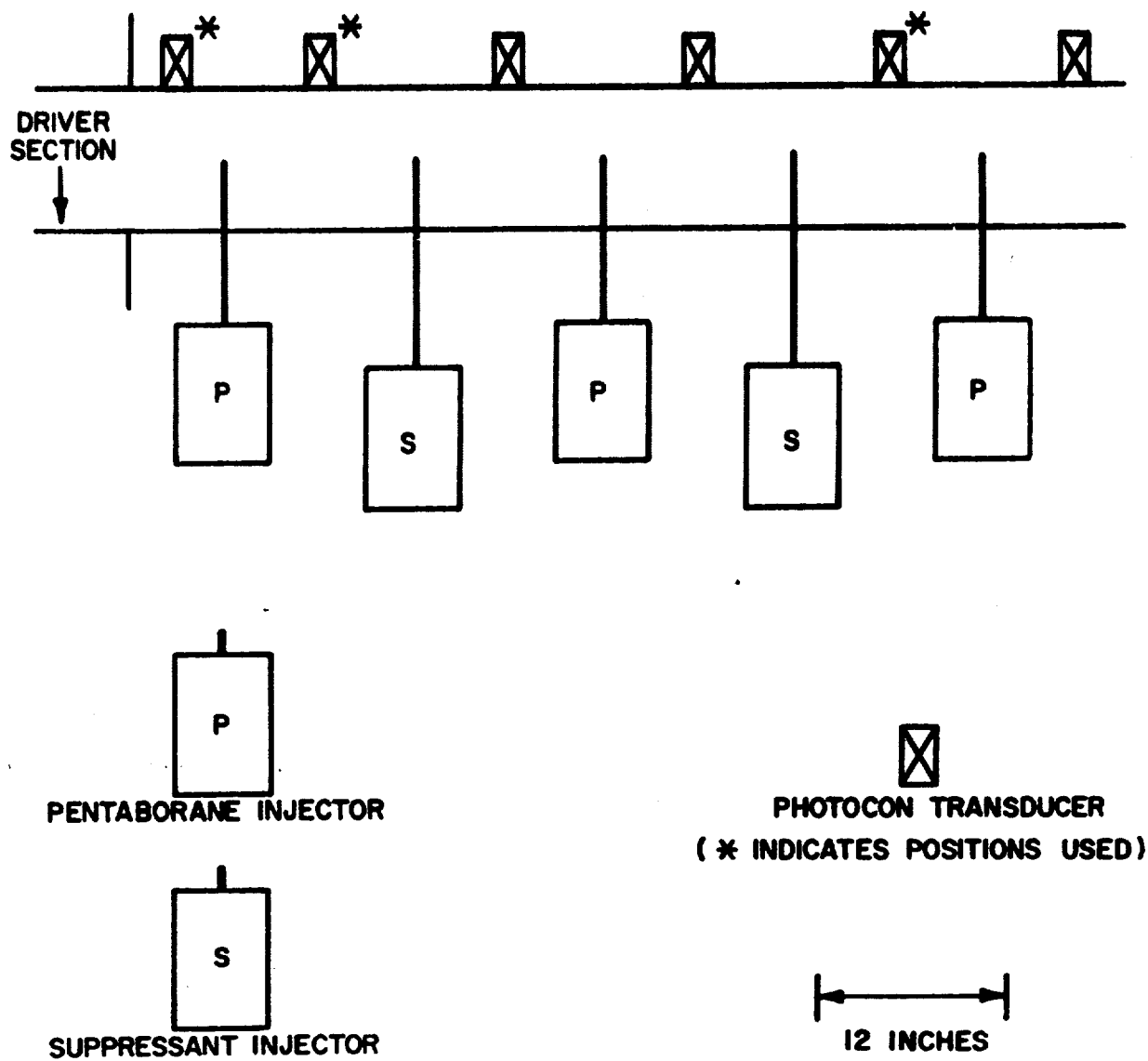
12 INCHES

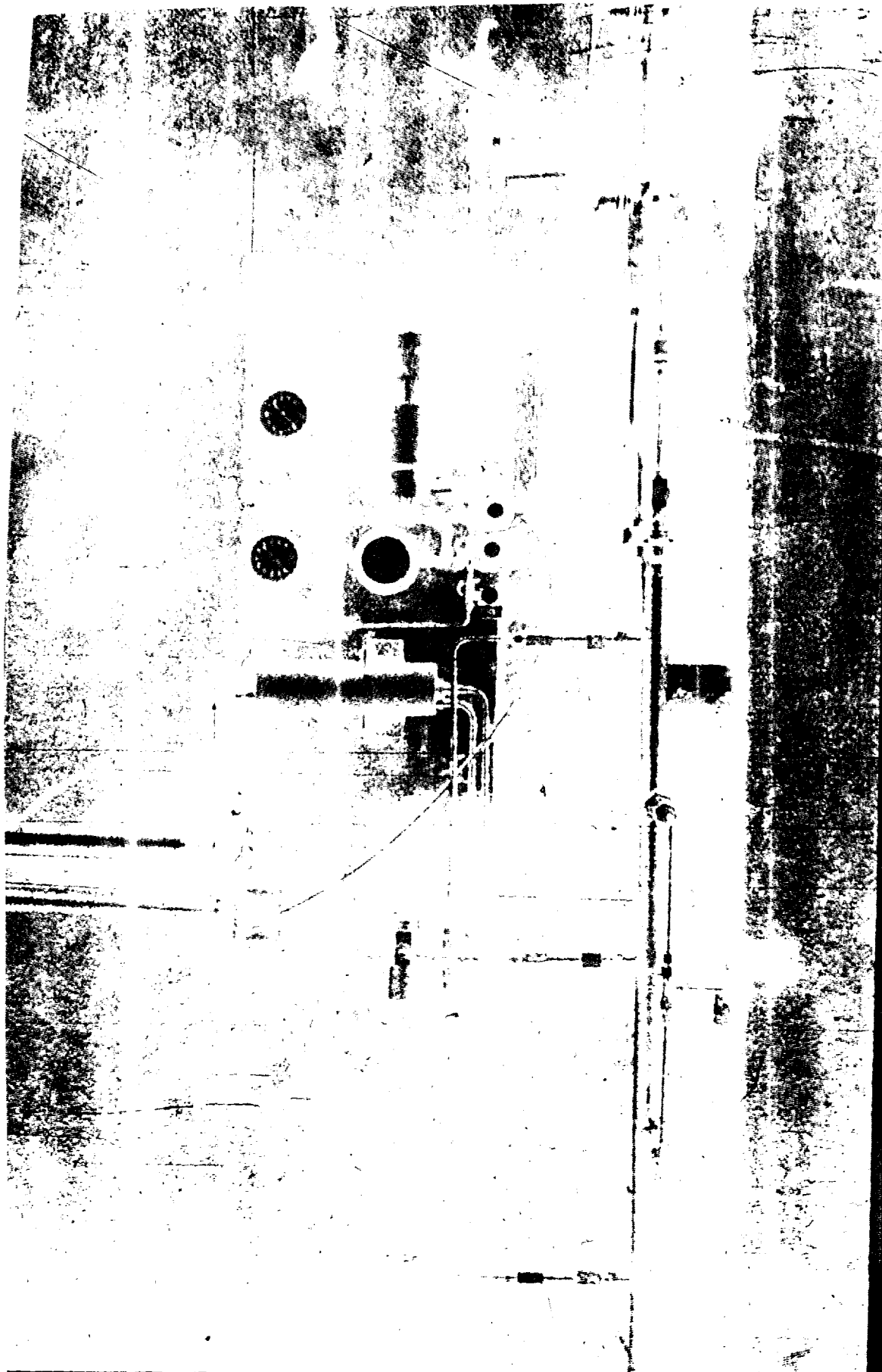Fig. 7. Schematic of Heterogenecus
Shock Tube

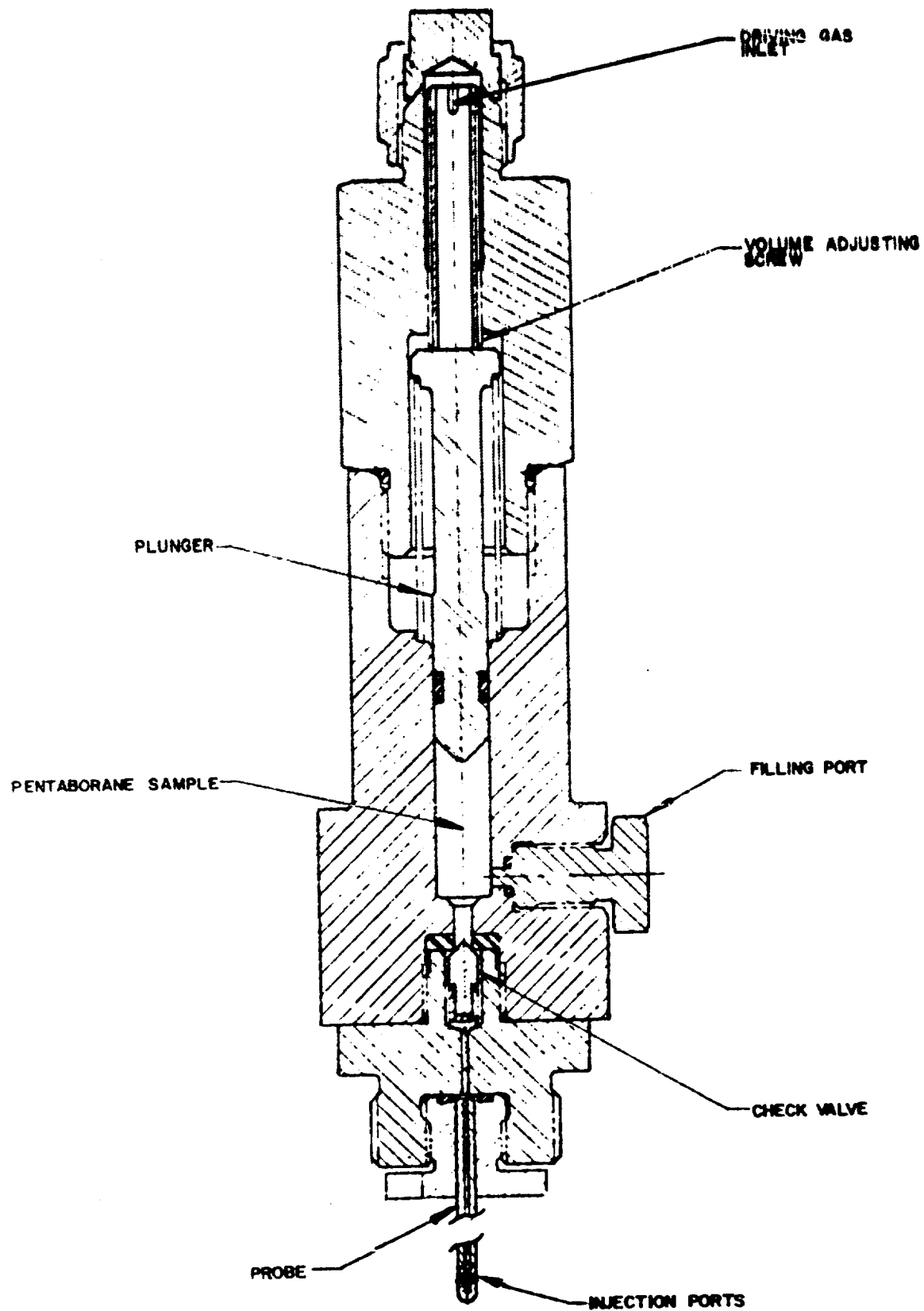Figure 8. Photograph of Shock Tube Installation

44

Figure 9. Shock Tube Injector

actuation and the application of nitrogen pressure, at 750 psig, to an injection manifold. Fuel and suppressant injection systems had separate manifolds.

Driving pulses were generated by spark ignition of a stoichiometric hydrogen-oxygen mixture. This explosive mixture was held in a cup slightly smaller in diameter than the shock tube proper and 1 inch in length. The face of the cup was covered with cellophane to retain the gas mixture prior to ignition. Hydrogen and oxygen were mixed in correct proportion in a separate 2-quart tank; once added to the tank, the gases were allowed to mix by diffusion over a period of several days. Each batch prepared in this way was sufficient for 8 to 10 shock tube tests. An annular passage around the driver gas cup provided an inlet for solid suppressants suspended in air and for the air purge that followed each test.

Solid suppressants were stored and fed from a hopper equipped with an electrical vibrator. Suspension in a carrier air stream was accomplished by means of a solids carburetor. A valve placed upstream of the carburetor was employed to pressurize the feed hopper. Actuation of a valve placed downstream of the carburetor introduced carrier air through a nozzle in the bottom of the hopper and gave the desired aspiration of suppressant. All of the explosion suppressants tested were readily conveyed to the shock tube with this system with the exception of urea. The latter tended to cake in the feed hopper. The addition of about one-third, by volume, of a high-surface, silica-alumina powder (CS-200 catalyst) to the urea overcame this difficulty.

Fuel injectors were filled in a glove box, under dry nitrogen, before installation into the shock tube. Two identical sets of injectors were available, and all tests were carried out in pairs to minimize setup time. Loading suppressants into the injectors or feed hopper, as appropriate, required no special procedures. The driver chamber was purged with about 10 times its own volume of hydrogen-oxygen mixture to remove air. Test sequencing was controlled with an Eagle automatic timer, and all pressure transducer outputs were recorded on magnetic

tape. Since three of the six transducer locations were used; these included the positions 3, 12, and 48 inches from the driver section flange, respectively. Following each test the apparatus was purged and cleaned; the cellophane diaphragm over the driver section was replaced. All pentaborane and suppressant injectors were disassembled and cleaned; in addition, new O-ring seals were installed for each test.

High-speed motion pictures were taken of injectors in operation with water and acetone as the test fluids. The purpose of these tests was to (1) evaluate stream breakup and droplet distribution and (2) obtain time relationships for use in setting test sequences. It had been planned to load each injector with exactly the quantity of pentaborane to satisfy the desired oxidation ratio; a dead space equivalent to 1-1/2 times the volume of the probe and check valve cavities and a relatively low injection pressure (150 to 200 psig) were planned, also. The motion pictures showed these conditions to be unsatisfactory; approximately the first half of the fuel was injected properly, but the remainder dribbled from the injection probe interspersed with gas bubbles. Higher driving pressures did not improve this situation. Finally, the injectors were adjusted to hold a volume of pentaborane equal to the volume to be used plus the volume of the probe and check valve cavities. Satisfactory injection resulted. Higher driving pressures gave better spray distribution and smaller droplets; however, the distance traversed by the droplets increased. At an injection driving pressure of 750 psig, the sprays carried over 2 feet. This pattern appeared acceptable, and a 750-psig injection pressure was used throughout the program.

Flow of pentaborane was observed to commence from 70 to 80 milliseconds after the signal to the pressurization valve to open; flow was complete about 130 to 150 milliseconds after the valve signal. The automatic sequencer was initially set to spark the hydrogen-oxygen driver mixture 250 milliseconds after the signal to the fuel injection valve. After test 25, this delay was reduced to 150 milliseconds. In both cases, delays were established with a clock which later was discovered to be in error. The 150-millisecond delay was checked on the oscillograph recording system and found to be 115 milliseconds. Delays reported for

test 25 and all subsequent tests were determined in this fashion. Unfortunately, the clock error was not reproducible. Therefore, the initial delay of 250 milliseconds could not be corrected, and values reported for tests 1 through 24 are approximate. In tests employing liquid suppressants, the suppressant was injected simultaneously with the pentaborane. In the case of solid suppressants, suppressant carrier flow was terminated 20 to 30 milliseconds prior to pentaborane injection; the duration of suppressant carrier flow was about 1 second.

RESULTS

Tests 1, 18, 19, and 23 employed the driver pulse only. The driver cup was purged twice as long prior to test 1 as for subsequent tests. There was some evidence that the driver pulse was stronger in this instance. Pressure records from test 1 were distorted by stray currents in the shock tube apparatus. Five of the first 11 tests were subject to this same difficulty; adequate grounding eliminated this problem entirely beginning with test 12. The results of tests 18, 19, and 23 were found to be quite consistent. Side-on or static pressures and transit times for the three transducer stations were as follows:

	Pressure, psig	Transit Time, milliseconds
Station 1	30 to 46	0.37 to 0.39 (1 to 2)
Station 2	23 to 29	2.28 to 2.33 (1 to 3)
Station 3	10 to 13	

where stations 1, 2, and 3 correspond to the ports at 3, 12, and 48 inches from the driver section flange, respectively.

Employing the postshock pressures noted in the preceding paragraph, pulse Mach numbers were computed from the normal shock tables of Ref. 42. The average Mach numbers for tests 18, 19, and 23 were converted to pulse velocities with a speed of sound of 1120 ft/sec. Arithmetic average pulse velocities for stations 1, 2, and 3 were 2030, 1800, and 1480 ft/sec, respectively. A graphical integration of these values

generated transit times of 0.395 milliseconds for stations 1 and 2 and
2.260 milliseconds for stations 1 and 3. Agreement with observed transit
times was excellent.

Sixteen tests were carried out with pentaborane and no suppressant.
Oxidation ratios of 0.25 to 1.00 were employed; subsequently, all sup-
pressant tests were performed at oxidation ratios of 0.33 and 1.00. In
two tests (runs 26 and 27 at an oxidation ratio of 0.33 and an electrical
delay of 115 milliseconds), more than five times the amplification of
the driver pulse took place between the driver section flange and the
first transducer port, i.e., in 3 inches. No growth period, such as ob-
served by Webber and Cramer, was detected. Slight additional amplifica-
tion accompanied passage of the amplified shock through the remaining
5 feet of tube. Total transit time between stations 1 and 3 was re-
duced from about 2.3 milliseconds for the driver pulse to 0.64 milli-
second for the amplified pulse. The stoichiometry of the heterogeneous
combustion field behind the shock cannot be described adequately to
make a comparison with a Chapman-Jouguet detonation wave. Finally, an
attempt to reproduce this behavior in tests 50 and 51 was unsuccessful.

In 13 tests of pentaborane without suppressant, at all oxidation ratios
and at electrical delays of 115 to about 250 milliseconds, the driver
pulse passed the heterogeneous field without behaving appreciably dif-
ferently than in air alone. Pulse pressure amplifications of 10 to
20% was encountered between stations 1 and 2; however, pulses were
attenuated, probably by simple viscous effects, between stations 2 and
3. Total transit times between stations 1 and 3 continued to be about
2.3 milliseconds. The driver section failed to ignite in one test.

Expulsion of pentaborane from the open end of the shock tube produced
a brilliant flash and audible report. As a direct consequence of this
external reaction, a pressure pulse of variable strength propagated
down the shock tube in the reverse direction. In most cases, i.e., 10,
this rearward pulse was amplified into a strong detonation wave before
reaching station 3. However, no amplification whatever was observed in
tests 4 and 9. In fact, the unamplified rearward wave was so weak as

to be undetectable. Periods of 0.8 to 5.5 milliseconds elapsed between the passage of the driver pulse as station 3 and the return of the rearward wave to the same position. All rearward-moving waves were attenuated in transit between stations 3 and 2. Results of tests of pentaborane without suppressant are summarized in Table 5. Figures 10 and 11 are oscillograph records of an amplified driver pulse and amplified rearward wave, respectively.

Six liquid suppressants were considered experimentally in a series of 15 shock tube tests. Results are summarized in Table 6. Suppressant ratio is the weight ratio of suppressant to pentaborane. At an oxidation ratio of 1.0, dimethyl sulfide, carbon tetrachloride, and acetonitrile gave no evidence of driver amplification or rearward wave propagation. Only the simple driver pulse and minor pressure disturbances were observed. At the same oxidation ratio, a solution of iodine in aqueous potassium iodide produced the only instance of pulse growth or slow driver amplification of the program. In a second test under comparable conditions, the driver pulse was fully amplified prior to reaching station 1. In one of two tests of trimethoxyphosphine, at this oxidation ratio, a rearward-propagating wave with a delay of 4.2 milliseconds at station 3 was observed. Slight fluctuations were observed in the other. Acetonitrile was tested twice at an oxidation ratio of 0.33. One immediate amplification and one returning amplification wave, with a station 3 delay of 0.8 milliseconds, occurred.

The reactivity of the pentaborane-acetonitrile spray mixture in tests 28 and 29 prompted a test of acetonitrile alone. It was of interest to determine whether any measurable reaction would follow passage of the driver pulse through a field of acetonitrile droplets. Test 33 was run at an oxidation ratio of 0.14, based on acetonitrile; the actual volume of fuel injected was the same as that employed as suppressant in tests 28 and 29. The presence of acetonitrile had no effect whatever on the driver pulse.

TABLE 5

SHOCK TUBE TESTS OF PENTABORANE ONLY

Run Number	Ignition Delay, milliseconds	Oxidation Ratio	Delay at Station 3, milliseconds	Remarks
2	~250	0.50	2.0	
3	~250	0.67	-	Stray current, no data
4	~250	1.00	-	Driver only, no rearward wave amplification
5	-	-	-	No ignition
9	~250	1.00	-	Driver only, no rearward wave amplification
17	~250	1.00	5.5	
24	~250	0.33	4.4	
25	~250	0.33	4.3	
26	115	0.33	-	Driver amplified
27	115	0.33	-	Driver amplified
30	115	0.50	4.0	
31	115	0.50	0.8	
48	140	0.25	3.7	
49	140	0.25	5.0	
50	140	0.33	5.2	
51	115	0.33	1.5	
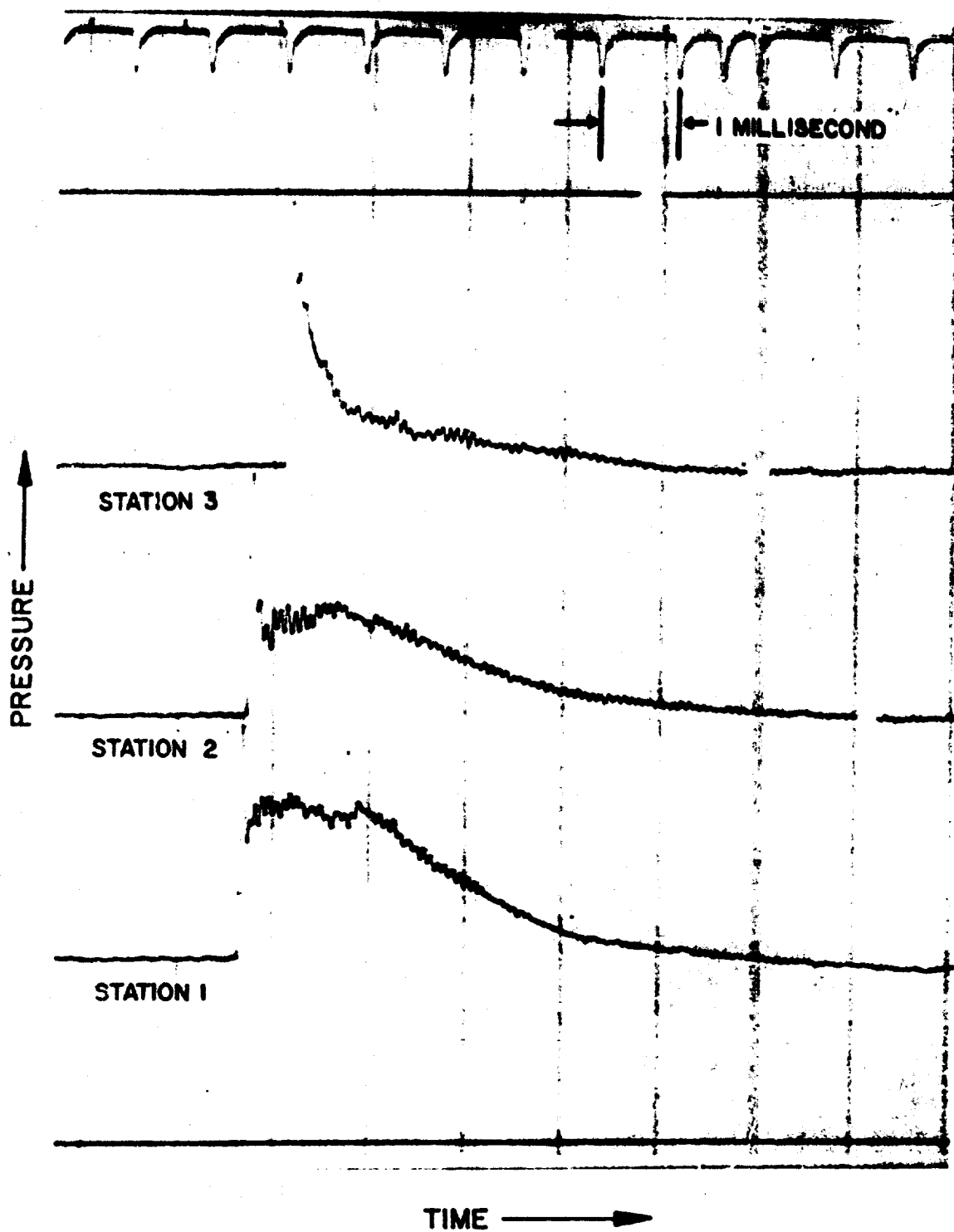
Figure 10. Amplified Driver Pulse (Test 26)
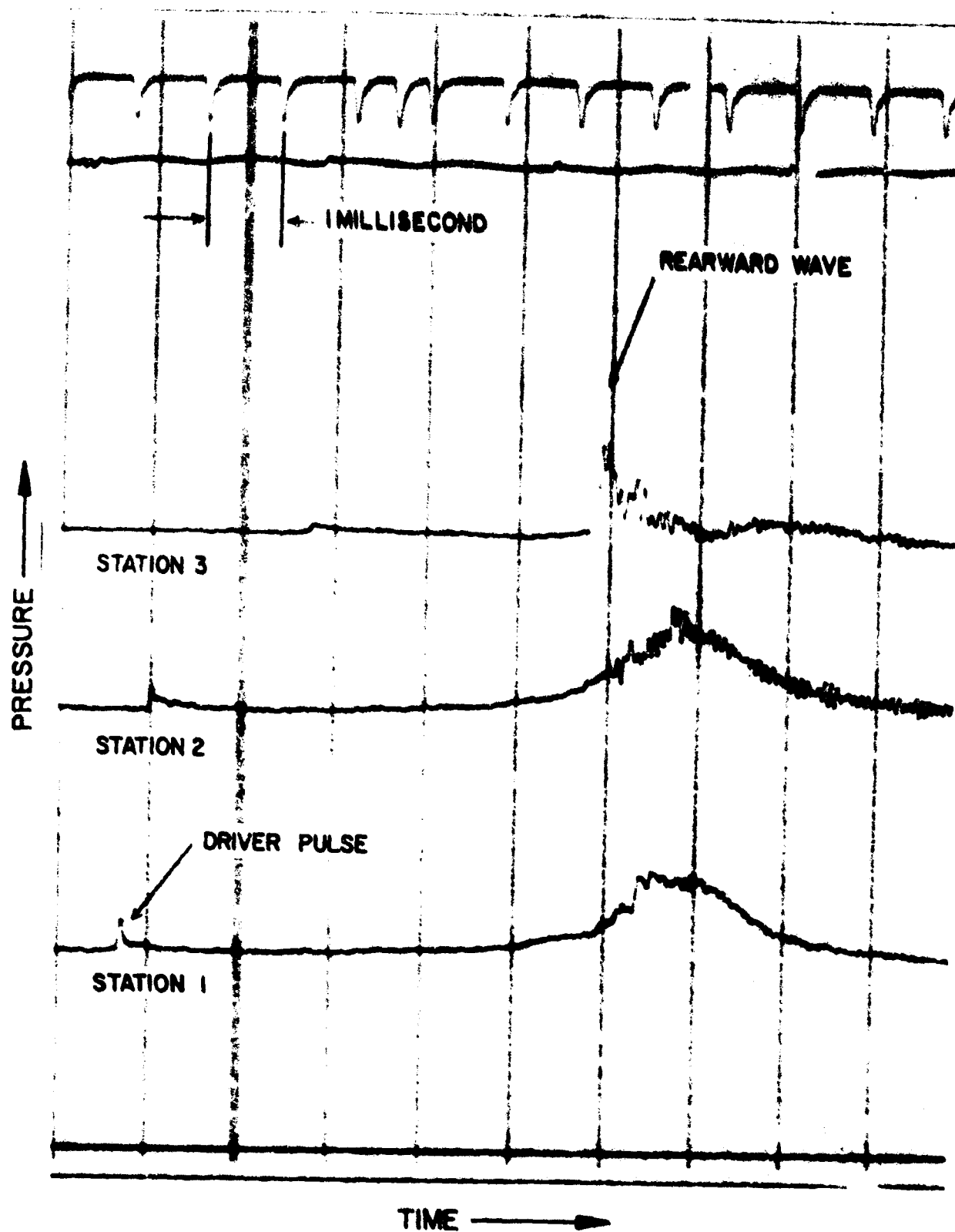
Figure 11. Amplified Rearward Wave (Test 48)

TABLE 6

SHOCK TUBE TESTS WITH LIQUID SUPPRESSANTS

Run Number	Ignition Delay, milliseconds	Oxidation Ratio	Suppressant Ratio	Suppressant	Remarks
6	~ 250	1.00	15.4	Carbon Tetrachloride	Driver pulse only
7	~ 250	1.00	20.0	Carbon Tetrachloride	Slight pressure disturbances
8	~ 250	1.00	8.7	Ethylenediamine	Stray current, no data
10	~ 250	1.00	8.7	Ethylenediamine	Stray current, no data
11	~ 250	1.00	11.5	Ethylenediamine	Stray current, no data
14	~ 250	1.00	7.5	Acetonitrile	Driver pulse only
15	~ 250	1.00	9.8	Acetonitrile	Driver pulse only
16	~ 250	1.00	15.0	I_2 + KI (aqueous)	Pulse growth, amplified driver
20	~ 250	1.00	19.5	I_2 + KI (aqueous)	Immediate amplification
21	~ 250	1.00	11.6	Trimethoxyphosphine	Slight pressure disturbances
22	~ 250	1.00	15.1	Trimethoxyphosphine	Rearward wave, delayed 4.2 milliseconds
28	115	0.33	3.3	Acetonitrile	Immediate amplification
29	115	0.33	3.3	Acetonitrile	Rearward wave, delayed 0.8 millisecond
32	115	1.00	8.1	Dimethyl Sulfide	Instrumentation failure
46	140	1.00	8.1	Dimethyl Sulfide	Driver pulse only
33	~ 250	-	-	Acetonitrile	No pentaborane, driver pulse only

Four solid suppressants were evaluated in 12 shock tube tests. Table 7 is a summary of these experiments. In preliminary tests, urea was found to easily clog the feed hopper and carburetor. A mixture of urea with 20% CS-200, high-surface, silicon-alumina powder (by weight) was transportable without excessive difficulty. CS-200 is a petroleum cracking catalyst; it has a very high surface area and was used to study the effect of solid interfaces as possible sites for chain-breaking reactions. In the first full tests of solid suppressants on pentaborane sprays, the entire shock tube filled with solids, and no useful data were obtained.

In addition to the urea-CS-200 mixture, boric acid, calcium carbonate, and neat CS-200 were investigated as detonation suppressants. Each of the four was run at an oxidation ratio of 1.00. All gave an unamplified driver pulse and very slight pressure disturbances at this oxidation ratio. The urea mixture, CS-200, and boric oxide were investigated at an oxidation ratio of 0.33, also. Test 45 with CS-200 gave an unamplified driver pulse. An amplified rearward wave, exhibiting a delay of 22 milliseconds at station 3, appeared in the case of boric oxide. Test 37 with the urea mixture gave a spurious pressure response that began at station 3 about 30 milliseconds after pulse. Pressure rise was gradual, unlike the sharp increase observed for rearward waves. Further, transit time to station 2 was greater than for the usual amplified rearward wave. It appeared to be part of a growth pattern for a returning pulse.

As noted earlier, the transit time for an unamplified driver pulse through the heterogeneous pentaborane-air field was equivalent to that for the driver pulse through air alone. With the addition of either a liquid or solid suppressant to the field, driver pulse transit times were increased. Both cases gave an average time of passage between stations 1 and 3 of 2.9 milliseconds. Variations around the average were greater for the liquid case. Thus , the injection of material, in addition to pentaborane, directly influenced driver pulse velocity; the pulse ceased to behave as if it were only in air.

TABLE 7

SHOCK TUBE TESTS WITH SOLID SUPPRESSANTS

Run Number	Ignition Delay, milliseconds	Oxidation Ratio	Suppressant	Remarks
34	140	1.00	Urea + CS-200	Shock tube filled with solids
35	140	1.00	Urea + CS-200	Shock tube filled with solids
36	140	1.00	Urea + CS-200	Driver pulse only
37	140	0.33	Urea + CS-200	Pressure pulse after 30 milliseconds
38	140	1.00	Boric Acid	Driver pulse only
39	140	0.33	Boric Acid	Rearward wave, delayed 22 milliseconds
40	140	1.00	Calcium Carbonate	No solid at ignition, slight pressure disturbances
41	140	0.33	Calcium Carbonate	solid at ignition, rearward wave delayed 5.5 milliseconds
42	140	1.00	CS-200	Driver pulse only
43	140	0.33	CS-200	No solid at ignition, rearward wave delayed 9.1 milliseconds
44	140	1.00	Calcium Carbonate	Slight pressure disturbance
45	140	0.33	CS-200	Driver pulse only

DISCUSSION

The combustion of pentaborane sprays in the presence of a traveling wave has been shown to be a complex process. Shock wave ignition is a function of oxidation ratio, shock properties, and delay between injection and ignition. The marked effect of oxidation ratio was anticipated on the basis of previous, heterogeneous, shock tube studies. However, the difficulty in initiating a detonation process in pentaborane droplets suspended in still air was not expected. A forward-moving driver pulse was amplified significantly in only two cases. In general, the driver pulse passed through the heterogeneous field without stimulating more than minor pressure disturbances. It is surprising that pentaborane in air is more difficult to initiate to detonation than kerosene in oxygen. This latter follows from comparison with the work of Webber and Cramer whose equipment and initiation techniques were very similar to those reported herein.

It is likely that the droplet breakup process hypothesized by Cramer takes place as the driver pulse moves down the shock tube. The result is a field of both macro- and micro-droplets of fuel at slightly elevated pressure and temperature. This picture of the field helps to explain the amplification of rearward waves. Reaction of pentaborane ejected from the open end of the shock tube produces a pressure pulse of variable strength. A portion of this pulse enters the shock tube and propagates in the reverse direction. As a consequence of the droplet shattering that has been assumed, a rearward wave is capable of initiating a stronger reaction than the original driver pulse. The rearward wave was highly amplified in all tests in which it could be detected at all. Thus, the returning pulse is capable of growth to a detonation wave as it traverses the tube.

In two of three tests with pentaborane at an oxidation ratio of 1.00 and delay of about 250 milliseconds, no rearward wave was observed. A third test produced an amplified rearward wave; the delay in reappearance at station 3, i.e., 5.5 milliseconds, was the longest of any

encountered with only pentaborane present. At lower oxidation ratios, either an amplified driver pulse or an amplified rearward wave was the result. The lack of reproducibility under duplicate test conditions was greater than the effect of delay time or oxidation ratio at these lower ratios. Rapid driver amplification occurred in two tests at an oxidation ratio of 0.33, yet this result was not achieved in test 51. Rearward waves with delays of 1.5 to 5.2 milliseconds were noted at this ratio.

The major influence of oxidation ratio is apparent. Other variations are the probable consequence of conditions at the ends of the shock tube. Driver explosive-mixture composition, spark characteristics, and cellophane closure properties are variables. Also, the location and rate of the combustion of expelled pentaborane will influence the initial magnitude and growth rate of rearward waves.

At an oxidation ratio of 1.00, dimethyl sulfide, acetonitrile, and carbon tetrachloride maintained an unamplified driver pulse when introduced simultaneously with the pentaborane. At the higher of two injection densities, trimethoxyphosphine generated a strong rearward wave. The lower injection density gave a negative response. Two tests with iodine in aqueous potassium iodide as the suppressant gave striking positive results. In the light of the tests without suppressant, at the same pentaborane oxidation ratio, negative results can generally be discounted. Amplified driver pulses and rearward waves are not to be expected with any great frequency. Thus, suppressant qualities for the first group of three agents noted above cannot be claimed with assurance. The result with trimethoxyphosphine must be viewed as marginal, while the iodine solution evidently acts as a sensitizer rather than a suppressant. This is an unexpected result; the increased ignition temperatures of iodine solutions in pentaborane, as discussed in an earlier section, suggest the opposite effect.

At an oxidation ratio of 0.33 and a delay of 115 milliseconds, acetonitrile gave an amplified driver pulse and an amplified rearward wave with a very short delay in two tests at different suppressant ratios. To determine whether the acetonitrile itself was detonating in response to the driver pulse, a test of acetonitrile at the same injection density and without pentaborane was carried out. There was no response but the normal, unamplified driver pulse. Acetonitrile is not a suppressant under shock tube conditions; it actually appears to further amplify the response of pentaborane alone. Thus, acetonitrile and iodine in aqueous potassium iodide have an adverse effect on the response of pentaborane sprays to shock initiation. The effects of the other liquid additives considered cannot be defined with confidence, since results fell within limits of experimental variation.

The case for the solid-phase additives is more promising. All solid suppressant tests were performed with an electrical delay of 140 milliseconds. No driver pulse amplification and no detectable rearward waves were observed with the urea mixture, boric acid, calcium carbonate, or CS-200 in a pentaborane droplet field at an oxidation ratio of 1.00. This result parallels the findings with liquid suppressants and, relative to tests with pentaborane alone, is equally inconclusive. However, shock tube behavior at an oxidation ratio of 0.33 is suggestive. Both the urea mixture and boric acid permitted the growth of rearward waves but, in both cases, delays measured at station 3 were quite long (22 and 30 milliseconds). Amplified rearward waves were not sharp as in previous cases. Finally, no positive reaction at all was encountered in the presence of CS-200. The long delay periods in the first cases are well beyond the limits of the tests with pentaborane alone. These solids therefore are contributing moderately to the suppression of detonation. On the other hand, CS-200 was wholly effective in preventing a positive response and is classed as an excellent suppressant.

The moderate efficiency of boric acid may serve to explain the attenuation of amplified rearward waves as they pass from station 3 to stations 1 and 2. The mild conditions produced by the driver pulse induce some combustion and formation of the related product specie, boric oxide.

As the rearward wave propagates back down the shock tube, it passes into material that has had longer and longer periods in which to react. As a consequence, the concentration of solid combustion product continuously increases. Either surface effects or specific third-body effects of boric oxide or boric acid are possible means of suppression and rearward wave attentuation.

The CS-200, silica-alumina powder has an order of magnitude greater surface area than the other solids tested. Silica-alumina may have a specific inhibiting effect on the pentaborane combustion process. However, with its great surface area, it may perform as a suppressant by simply providing an abundance of sites for recombination and chain-breaking reactions. Data are not sufficient to indicate which of these two possible roles is correct. In brief, the suppressant qualities of three solid substances have been demonstrated. The best of the three, a high-surface, silica-alumina powder, was capable of hindering wave amplification completely.

DECONTAMINATION STUDIES

APPARATUS AND PROCEDURE

The reaction vessel for decontamination studies was a 500-milliliter, two-necked, pyrex flask. Each neck was fitted with a stopcock to provide closure for the vessel during loading and sampling. Decontaminant solutions were introduced through one of the stopcocks from a 200-milliliter pyrex flask, in the manner of a dropping funnel. Decontaminant feed flasks were pressurized slightly to give smooth, rapid transfer. Gas generated by decontamination reactions was removed through the second of the stopcocks and passed to a conventional wet-test meter. Gas evolution was expected to provide the agitation necessary for mixing of pentaborane and decontaminant solution. However, the results of the first five tests indicated that this was not the case. Subsequently, mechanical agitation was applied with a Teflon-coated bar magnet placed in the reaction flask and rotated by means of a second, external bar magnet.

The decontamination reaction flask was immersed in a constant-temperature bath. At superambient temperatures, bath temperature was controlled solely with electrical heaters. Under subambient conditions, an excess of chilled trichloroethylene prepared in a commercial refrigeration unit was circulated through a coil of copper tubing in the bath; temperature control was achieved with the electrical heaters in this case, also. In most tests, temperature stayed within 1 F of the set point.

A measured volume of pentaborane (2 or 4 milliliters) was injected into the reaction flask, under a pure nitrogen atmosphere, in a glove box. Stopcocks were closed, and the flask was removed from the glove box to the constant-temperature bath. The exhaust line to the wet-test meter was purged with nitrogen and connected to the exhaust cock of the flask. A 200-milliliter flask containing decontaminant solution, pressurized to about 10 psig with nitrogen, was attached to the second cock. In turn, the exhaust cock and the decontaminant inlet were opened to begin

the test. In the first 13 tests, durations were limited to about 1 day; the volume of evolved gas was observed after 1 hour, 4 hours, and at the end of the test. Later tests were run until the evolution of gas had ceased, for all practical purposes.

In most cases, termination of a test was followed by the addition of 35% hydrochloric acid in the same way as the addition of decontaminant solution. Acid was added in small, equal portions until the evolution of gas was complete; the total increment of evolved gas was measured with the wet-test meter. The intent was to add sufficient acid to ensure complete hydrolysis of any hydride remaining in solution. Tests 12 and 14 were an exception; since very little reaction was noted on the first addition of acid, no additional portions appeared necessary, and a strongly acid condition was not achieved.

RESULTS

The total evolution of gas expected from these tests was based upon the ultimate, strongly acid state. Over-all reactions describing the hydrolysis or alcoholysis of pentaborane, in the presence of strong acid, can be written, as follows:

$$B_5H_9 + 15\ H_2O \longrightarrow 5\ H_3BO_3 + 12\ H_2 \tag{22}$$

$$B_5H_9 + 15\ CH_3OH \longrightarrow 5\ (CH_3O)_3\ B + 12\ H_2 \tag{23}$$
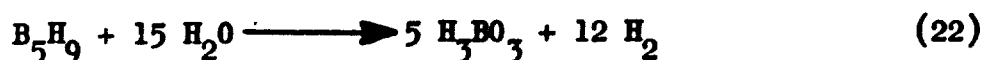
Thus, 12 moles of hydrogen gas are predicted for every mole of pentaborane oxidized in this way. In all but one test, 2 milliliters or 1.24 grams of pentaborane were loaded in the reaction flask. This quantity of liquid sample corresponds to 0.0193 gm-mole of pentaborane, or by reaction 22 or 23, to 0.232 gm-mole or hydrogen. Thus, a theoretical gas evolution of 0.187 cu ft hydrogen (0 C and 1 atm) can be calculated. Converting to average ambient conditions at the laboratory site yields a total expected evolution of 0.208 cu ft hydrogen (16 C and 0.95 atm). The vapor pressure of water at 16 C is approximately 13 mm Hg. If

saturation is assumed, the rounded, theoretical gas evolution is 0.21 cu ft per 2-milliliter sample. The volume of evolved gas indicated on wet-test meter was divided by this quantity (except run 27) to obtain the fraction of theoretical hydrogen for the particular observation.

The compositions of decontaminant solutions are summarized in Table 8; the results, arranged in chronological order, are summarized in Table 9. Measured gas volumes are reported in Table 9 as percentages of theoretical hydrogen.

As noted above, mechanical agitation was not applied in tests 1 through 5. The inconsistencies in the results of tests 2 through 5 led immediately to the conclusion that reliance on agitation by evolved gas was inadequate. Commencing with test 6, mechanical agitation was employed. The erratic result of test 6 was subsequently attributed to a leaking stopcock which permitted the escape of hydrogen gas. In brief, no real value can be placed on the observations from the initial six tests.

Acidification of the reaction residue was incomplete in tests 12 and 14. The addition of more acid to an aliquot of the residue from test 14 yielded an additional 17% of the theoretical hydrogen. Mass spectrometric analysis confirmed that gas evolved in the laboratory was pure hydrogen. As a check on a strongly acidified residue, additional acid was added to an aliquot from the residue of test 15; no further hydrogen was evolved. Similar laboratory experiments were performed on the residues from tests 16 and 17, neither of which had been acidified prior to sampling. The relatively neutral residue from test 16 evolved no gas when acidified in the laboratory, while the alkaline residue from test 17 yielded 33% of the theoretical hydrogen upon the addition of sufficient hydrochloric acid to produce a strongly acid condition. These results emphasize the importance of pH in the oxidative destruction of pentaborane by hydrolysis or alcoholysis.

TABLE 8

COMPOSITION OF DECONTAMINATION SOLUTIONS

Number	Composition, weight percent
1	Ammonia, 3.0; Aquet, 0.1; Water
1a	Ammonia, 3.0; Water
2	Ammonium chloride, 20.0; Aquet; 0.1; Water
3	Methanol, 20.0; Aquet, 0.1; Water
3a	Methanol, 20.0; Water
3b	Methanol, 16.4; Aquet, 0.1; Water
3c	Methanol, 16.4; Water
3d	Solution No. 3a acidified with 10% hydrochloric acid
4	Methanol, 20.0; Ammonia, 3.0; Water
5	Dioxane, 10.0; Water
5a	Dioxane, 20.0; Water
6	Methanol
7	Water
8	Isopropanol, 75.2; Hexylamine, 24.8
9	Ethylene glycol, 78.9; Ethylene diamine, 21.1
10	Ethylene glycol, 15.8; Ethylene diamine, 4.2; Water
11	Dioxane, 10.0; Sodium Hydroxide, 2.0; Water
12	Methanol, 20.0; Sodium Hydroxide, 2.0; Water
13	Sodium Hydroxide, 2.0; Water

NOTE: Aquet is a 25%, nonionic solution of an alkylarylpolyethyleneglycol marketed by the Manostat Corporation

Run Number	Decontaminant Solution	Weight of Decontaminant, grams	Weight of Pentaborane, grams	Bath Temperature, F	Run Duration, hours	Gas Evolution, % of Total Hydrogen		
						1 Hour	4 Hours	24 Hours
1	1	50	1.24	75	24	18	24	31
2	3b	48	1.24	80	24	--	6	16
3	3c	48	1.24	82	~4	27	~36	--
4	3c	48	1.24	82	3	16	--	--
5	3c	48	1.24	32	--	1	--	6
6	3c	96	1.24	67 to 85	21	14	--	--
7	1	100	1.24	80	22	15	14	--
8	8	78	1.24	83	1	29	20	--
9	1a	100	1.24	83	22	19	--	--
10	7	100	1.24	83	71	26	24	--
11	5	100	1.24	84	23	25	34	--
12	9	107	1.24	84	22	26	32	--
13	2	100	1.24	84	23	--	36	--
14	10	106	1.24	80	99	14	32	38
15	7	100	1.24	80	120	--	--	--
16	3a	100	1.24	80	72	27	25	32
17	1a	100	1.24	80	71	11	34	41
18	1a	100	1.24	40	140	--	19	--
19	3a	100	1.24	40	69	--	21	30
20	6	100	1.24	40	<1	--	43	54

*Acid plus 15-milliliter dioxane
**Acid plus 10-milliliter dioxane

TABLE 9

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DECONTAMINATION TESTS

1 Hour	% of 4	Gas Evolution, % of Total Hydrogen			% Gas Evolved from Acidification	Total Gas Evolved, % of Total Hydrogen	Remarks
		4 Hours	24 Hours	Total			
18		24	31	31			No stirring
--		6	16	16			No stirring
27		~36	--	~36			No stirring; stopcock failed after 4 hours
16		--	--	19			No stirring
1		--	6	--			No stirring
14		14	--	14			No stirring; leakage after 1 hour
15		20	--	22			
29		--	--	29	31	60	
19		24	--	27			
26		34	--	52	2*	54	
25		32	--	39	0	39	
26		36	--	43	3	46	Incomplete acidification
--		32	--	42	0	42	
14		--	38	54	4	58	Incomplete acidification; 17% more gas in laboratory
--		25	32	48	2**	50	No gas evolution in laboratory
27		34	41	50			No gas evolution in laboratory
11		19	--	29			33% more gas in laboratory
--		21	30	33			
--		43	54	57			
--		--	--	--			Very rapid reaction

2

TABLE 4

(Continu-

Run Number	Decontaminant Solution	Weight of Decontaminant, grams	Weight of Pentaborane, grams	Bath Temperature, F	Run Duration, hours	Gas Evo % of Tota	
						1 Hour	4 Hour
21	7	100	1.24	40	142	--	--
22	3	100	1.24	40	72	25	57
23	4	100	1.24	40	72	16	24
24	3d	100	1.24	40	46	24	53
25	3d	110	1.24	40	47	30	55
26	1a	100	1.24	40	50	13	--
27	3a	150	2.48	36 to 43	91	20	55
28	12	100	1.24	40	95	7	19
29	5a	100	1.24	39	26	33	63
30	11	100	1.24	40	95	7	--
31	13	100	1.24	70 to 90	75	11	25

1

TABLE 9
(Continued)

TABLE 9
(Continued)

Gas Evo of Tota 4 Hour	Gas Evolution, % of Total Hydrogen			% Gas Evolved from Acidification	Total Gas Evolved, % of Total Hydrogen	Remarks
	4 Hours	24 Hours	Total			
--	--	55	67			
57	57	61	61	0	61	
24	24	--	29	52	81	
53	53	61	61	1	62	
55	55	62	63			
--	--	29	30	52	82	
55	55	60	61	0	61	
19	19	39	48	50	98	
63	63	66	66	1	67	
--	--	41	54	44	98	
25	25	35	44	50	94	

2

The gas evolved when 35% hydrochloric acid was added to mixtures of
pentaborane and decontaminant solution is noted in column 11 of Table 9.
In most cases, acid was added after initial gas evolution essentially
had stopped. Reactions were quite violent and complete within 1 hour.
The time to complete gas evolution was reduced when the initial portion
of acid was sufficient to produce an over-all acid condition.

Total gas evolutions, with and/or without additional hydrochloric acid,
are reported in columns 10 and 12 of Table 9. In most cases, these
totals are well below 100%. One of the major factors contributing to
reduced gas evolution was the volatility and continuing vaporization of
pentaborane. The latter was present, frequently, as an immiscible liquid
phase and could exert its full vapor pressure as a consequence. Penta-
borane has vapor pressures of 80 to 225 mm Hg, respectively, at 40 and
80 F. Where gas evolution was slow and vapor-liquid equilibrium might
have been approached, as much as 30% of the gas leaving the reaction
flask could have been pentaborane. This condition was limited by (1)
complexing, appreciably reducing the equilibrium vapor pressure, as
well as (2) the relatively slow approach of liquid systems to vapor-
liquid equilibrium. Vaporization of pentaborane from the hot mixture
remaining after a fire is, of course, undesirable. Therefore, the
apparent loss of boron hydride is a significant factor in the evaluation
of a decontaminating agent.

The results of tests with aqueous ammonia are plotted in Fig. 12; the
decontaminant solution numbered 1a in Table 8 and noted as a cross in
the figure is the material employed by several agencies as a decontamin-
ating wash. Initially, relatively rapid gas evolution was observed for
all five tests; 1-hour yields varied from 11 to 19% of theoretical.
After 1 hour the rate decreased sharply. Gas evolution was complete,
for all practical purposes, after 24 hours; an observation made after
140 hours showed little change. All mixtures approached a limiting gas
evolution amounting to about one-third of the theoretical hydrogen.
Temperature and detergent content had no significant influence on the
results. Total gas yields of 62 and 82%, following final acidification,
were obtained in tests 17 and 26, respectively. The higher yield at
the lower temperature, i.e., 40 F in test 26, was consistent with the
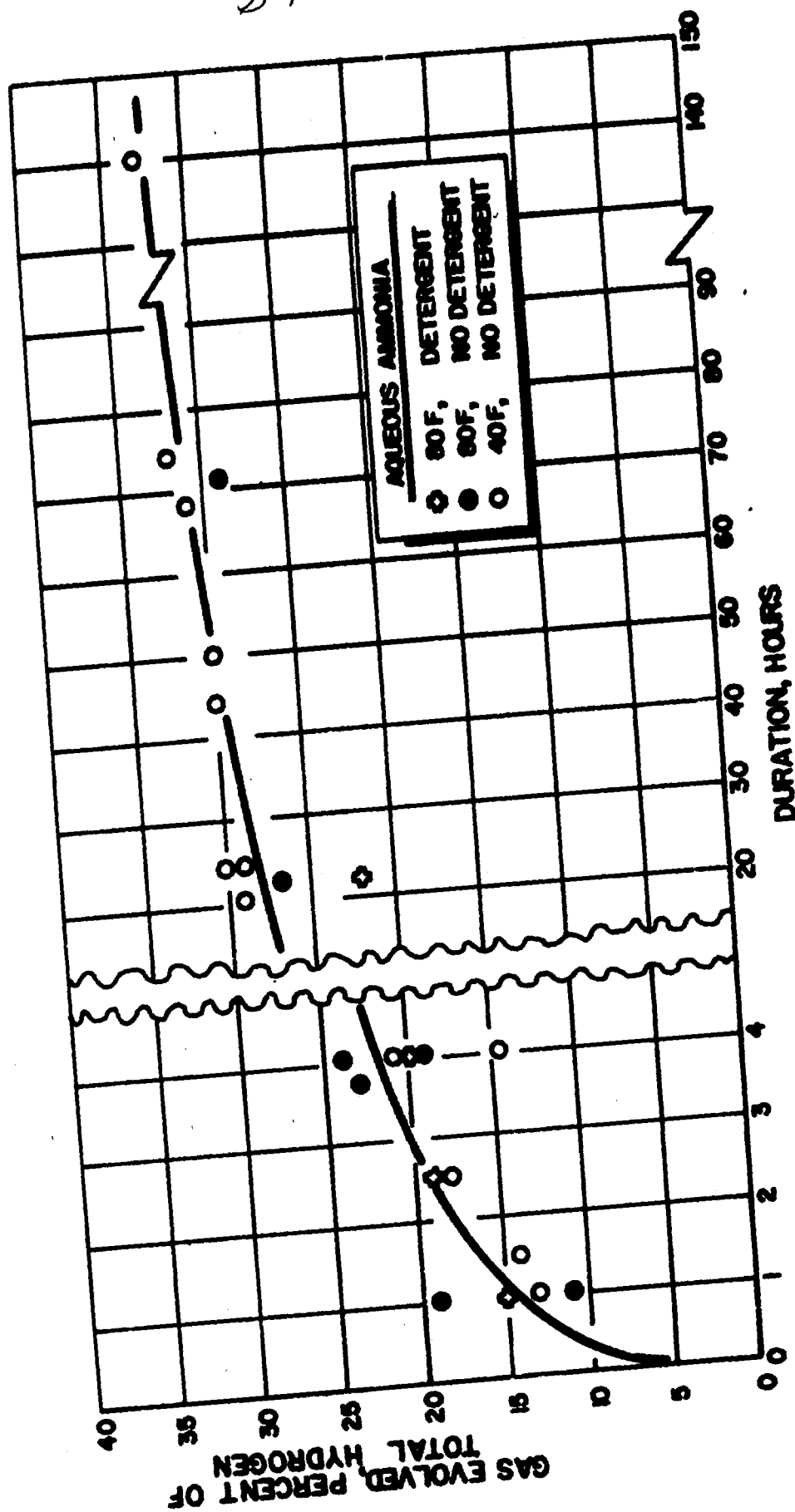loss of pentaborane through vaporization.

Figure 12. Gas Evolution from Aqueous Ammonia Decomposition

GAS EVOLVED, PERCENT OF TOTAL HYDROGEN

DURATION, HOURS

AQUEOUS AMMONIA

80F, DETERGENT
80F, NO DETERGENT
40F, NO DETERGENT

In the case of aqueous methanol, initial rates of gas evolution were higher and remained higher through the first 4 hours (refer to Fig. 13). Here, also, there was little evidence of gas evolution after the first 24 hours. Tests at 40 F reached a total gas volume corresponding to 60% of the theoretical hydrogen; the presence of detergent had no effect on the result. At 80 F, the rate of evolution was less, and the final volume was closer to 50% of the theoretical. The addition of acid at the conclusions of tests 16, 22, 24, and 27 yielded no further gas. Thus, all pentaborane had been destroyed or lost through vaporization. At the higher test temperature, the loss of pentaborane by vaporization was greater and led to smaller total gas evolution. Even at 40 F, about 40% of the initial charge was dissipated through vaporization.

Decontaminant solution 4 was prepared with the same methanol concentration as employed in the aqueous methanol decontaminant solutions 3, 3a, and 3d; in addition, it had ammonia in concentration equal to decontaminants 1 and 1a. Solution 4 behaved exactly as an aqueous ammonia solution; note correspondence between tests 23 and 26. About 30% of the theoretical hydrogen was observed during the test, while the total gas evolved reached 81% after acidification. Thus, vaporization losses were less than 20%. Complex formation makes a far greater contribution than alcoholysis in alkaline solution; it appears that methanol has a negligible effect when in the presence of ammonia. Pure methanol reacted violently with pentaborane in test 20; several joints were opened by the pressure in the reaction flask, and no useful measure of evolved gas volume was possible.

Pure water was comparable to aqueous methanol in most respects. The average gas volume at 80 F was 50% of theoretical; acidification gave no further gas. At 40 F, the volume of gas generated reached 67%. Greater gas evolution at the lower temperature again implies a smaller loss of pentaborane by vaporization. The major difference between water and aqueous methanol was the greater rate at which gas was evolved in the presence of 20% methanol.
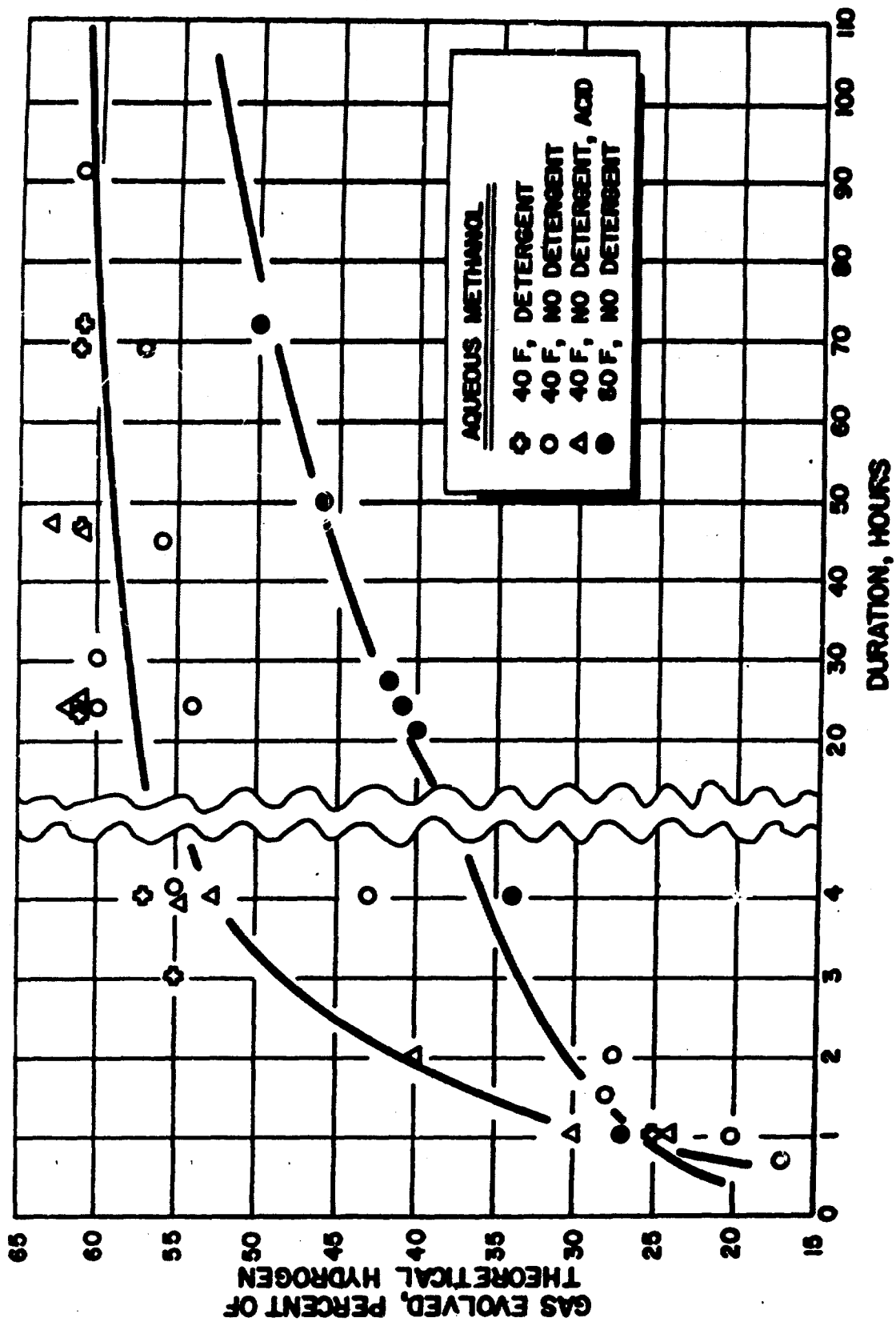
Figure 13. Gas Evolution from Aqueous Methanol Decomposition

A solution of 10% dioxane in water, at 80 F, was significantly poorer than either water or aqueous methanol. Only 39% of the theoretical hydrogen was observed; further, the apparent vaporization loss was the largest of any test. A similar experiment with a 20% ammonium chloride solution was equally poor. However, a solution of 20% dioxane in water, at 40 F, was as effective as water or aqueous methanol in the destruction of pentaborane and prevention of vaporization losses when compared under the same conditions.

The results for decontaminant solutions 8, 9, and 10 were inconclusive. However, the observations on dilute sodium hydroxide and solutions of dioxane (11) and methanol (12) in dilute sodium hydroxide were unique. The initial rate of decomposition of pentaborane in these solutions was the least of any of the decontaminants tested. In all cases, the rate increased during the first day; gas evolutions reached about 40% at the end of 24 hours. Within 4 days, gas volumes equivalent to 50% of the theoretical hydrogen had been collected. Of greatest significance, however, was the collection of nearly 100% of the theoretical quantity of gas upon final acidification of these mixtures. Although decomposition of pentaborane in the first few days exceeded that for the alkaline decontaminants containing ammonia, solutions 11, 12, and 13 hindered vaporization quantitatively. This effect is attributed to solubility effects and/or the formation of nonvolatile complexes that hydrolyze at some finite rate under alkaline conditions.

DISCUSSION

The action of the decontaminant solutions studied during this series of tests can be separated into several rather distinct categories. Practical application of decontaminants will rest upon the particular action that is desired in the light of immediate field or laboratory conditions. One class of decontaminants is that which destroys pentaborane quantitatively and very rapidly, without appreciable vaporization of boron hydride. Methanol, i.e., solution 6, is representative of this class. The rapid destruction of pentaborane is, of course,

accompanied by hydrogen evolution at an equal rate. Where the pentaborane is present in substantial quantity, this method of treatment would be undesirable as it creates a fire and/or explosion hazard. However, this method does appear to be suited to the elimination of toxicity hazard in association with only small quantities of pentaborane.

A related class of decontaminants includes those that destroy pentaborane at a somewhat slower rate. Neutral or acid solutions of methanol or dioxane in water (solutions 3 and 3a) and pure water (solution 7) destroyed pentaborane over a period of 4 to 24 hours. Pentaborane exerts an appreciable vapor pressure in mixture with these solutions; therefore, vaporization continues until the former is eliminated entirely. Although hydrogen evolution is slowed, a toxicity hazard persists until destruction of pentaborane is complete. It is noteworthy that the effect of 20%, by weight, methanol or dioxane is not especially large. The superiority of the organic solutions relative to pure water was modest and probably of the same order of magnitude as the experimental error.

Alkaline solutions of methanol and dioxane in dilute sodium hydroxide or aqueous ammonia are indistinguishable from the basic alkaline solutions. The alkaline solutions studied during this program can be divided into two classes; a group based on sodium hydroxide and a group based on ammonia. Dilute sodium hydroxide or solutions of methanol or dioxane in dilute sodium hydroxide; i.e., solutions 11, 12, and 13 appeared to solubilize and/or complex pentaborene readily. This effect was sufficiently rapid to prevent loss of boron hydride through vaporization. Oxidation of pentaborane in these solutions continued, but at a very reduced rate; thus, pentaborane persists in these solutions in a semi-stable form. Rates of hydrogen evolution appear to be tolerable for the majority of possible application. The addition of sufficient acid to neutralize these solutions frees pentaborane, increasing the rate of oxidation and permitting some vapor loss as well. It must be emphasized that the addition of oxidizing organics to dilute sodium hydroxide has a negligible effect.

Water and neutral or acid solutions of organics will be of maximum value where rapid, but controlled, elimination of pentaborane is desired. Both hydrogen and pentaborane vapor are present; therefore, these decontaminants would require adequate ventilation. The use of alcohol or dioxane is of limited value in 20% concentration. However, higher concentrations that do not exceed the flammability limit of the organic solution per se are probably worthy of consideration for some applications in which the speed of pentaborane destruction is critical.

Dilute sodium hydroxide solutions are applicable to situations in which the fire and toxicity hazards of hydrogen and pentaborane vapor are not tolerable and speed is not critical. The concept of secondary treatment applies to this class of decontaminant, also. If the mixture of pentaborane and decontaminant solution is transferred from the treatment site to a suitable collecting sump, ditch, etc., a secondary treatment with acid can be employed safely to speed oxidation of the borane.

The complexing action of ammonia and organic amines on the boron hydrides is well known. Experiments with aqueous ammonia solutions (1 and 1a) indicated that this effect is not as efficient as was expected. Very stable, water-soluble complexes are formed; however, these reactions are slow, as indicated by the evolution of about 30% of the theoretical hydrogen and vaporization losses, amounting to approximately 20%. The advantage of this class of decontaminants lies in the stability of the resulting complexes, which can be retained for long periods without serious hazard and disposed of when convenient. Secondary treatment with acid is a satisfactory method of destruction. The disadvantage of ammonia solutions arises from the evolution of moderate amounts of hydrogen and borane vapor that accompany their application. In general, this class of decontaminant solutions appears applicable to the same situations as the dilute sodium hydroxide solutions. Further, the use of organic additives is equally unnecessary.

CONCLUSIONS AND RECOMMENDATIONS

It has been conclusively shown that pentaborane-air fires can be suppressed
by chemical means. The dramatic effect of methyl iodide and, to a lesser
extent, dimethyl sulfide in putting out the flame in the diffusion burner
strongly indicates that a practical chemical extinguishant for pentaborane
fires exists. Additional investigations, both in a diffusion burner and
on pool fires, will be required to develop the optimum extinguishant.
Primary candidates for investigation are organic iodides, bromides, and
solutions of iodine in organic carriers, especially halogenated compounds.
Studies with organic sulfides and polysulfides would also be desirable
(at least from a scientific standpoint, if not from a practical standpoint).

The marked differences in effectiveness of different compounds strongly
supports a chain-branching mechanism for the combustion of pentaborane
in air. If combustion were propagated by a purely thermal mechanism,
any inhibition would be the result of dilution since latent heat effects
were essentially removed by prevaporization of the suppressant. In this
case, the inhibition should be proportional only to the mole concentra-
tion of the diluent. It is hypothesized that the iodine atom from methyl
iodide reacts with borane radicals to form a relatively stable entity,
thereby breaking the chain reaction. The CH_3S radical from dimethyl
sulfide, on the other hand, probably breaks the chain by reacting with
oxygen atoms.

Because of the complexity of the results obtained in the explosion
burette, definite conclusions cannot be drawn about most of the materials
tested. No suppressant action could be attributed to any of the liquids
tested; however, an aqueous solution of iodine and potassium iodide
definitely enhanced the propagation of pentaborane-air explosions. This
was attributed to the presence of water, which masked any inhibition
caused by the iodine. It appeared that acetonitrile might also act as
a weak sensitizer.

A high-surface-area, silica-alumina powder definitely acted as a suppressant for the pentaborane-air detonation. This effect was attributed to the high surface area and thus was more physical than chemical in nature. Results with the other solid suppressants tested were inconclusive.

It is felt that, in spite of the limited results obtained, the heterogeneous shock tube is a valuable tool for the investigation of explosion suppression by chemical techniques. The first step in any further work would be the thorough investigation of the reaction of heterogeneous pentaborane-air mixtures to shock ignition. This would provide a much firmer basis for the selection of conditions and interpretation of results in a test program designed to evaluate candidate explosion supressants. The effects of water and the compounds which gave promising results in the diffusion burner could then be investigated. In the case of solids, the effects of surface area and chemical composition could be profitably investigated.

The wide range of results from the pentaborane decontamination studies suggests the important possibility of "tailoring" a decontamination solution to meet the conditions and limitations of a specific situation. Decontamination solutions which produce results ranging from immediate destruction of the pentaborane to retention of the pentaborane in solution with very little decomposition were tested. Further investigation would be required for optimization of decontamination solutions. However, the present work provides guidelines for the selection of decontamination solutions for immediate use and further study.

REFERENCES

1. Friedman, R., and Levy, J. B., _Survey of Fundamental Knowledge of Mechanisms of Action of Flame-Extinguishing Agents_, Atlantic Research Corporation, WADC TR-56-568, ASTIA No. AD-110685 January 1957.

2. Friedman, R., and Levy, J. B., _Survey of Fundamental Knowledge of Mechanisms of Action of Flame-Extinguishing Agents: First Supplementary Report_, Atlantic Research Corporation, WADC TR-56-568, ASTIA No. AD-208317, Sept. 1958.

3. Friedman, R., and Levy, J. B., _Survey of Fundamental Knowledge of Mechanisms of Action of Flame-Extinguishing Agents: Second Supplementary Report_, Atlantic Research Corporation, WADC TR-56-568, ASTIA No. AD-216086, May 1959.

4. Young, H. H., and Eggleston, L. A., _Study of Fire Extinguishing Agents and Preventative Techniques for High Energy Fuels_, Midwest Research Institute and U. S. Fire Protection Engineering Service, Inc., WADC TR-59-334, ASTIA No. AD-227965, May 1959.

5. Lewis, B., and Von Elbe, G., _Combustion, Flames and Explosions of Gases_, Academic Press, Inc., 1961.

6. Rosser, W. A., Inami, S. H., and Wise, H., _Study of the Mechanisms of Fire Extinguishment of Liquid Rocket Propellants_, Stanford Research Institute, WADC TR-59-206, ASTIA No. AD-216355, April 1959.

7. Belles, F. E., "Chemical Action of Halogenated Agents in Fire Extinguishing," NACA, TN-3565, September 1955.

8. Thomas, C. A., and Hochwalt, C. A., "Effect of Alkali-Metal Compounds on Combustion," Ind. & Engr. Chem., Vol. 20, No. 6, 575, June 1928.

9. Levy, J. B., and Friedman, R., _Study of the Mechanism of Flame Extinguishment by Aluminum Chloride_, Atlantic Research Corporation, WADC TN-58-1, ASTIA, No. AD-142271, October 1957.

10. Willbourn, A. H., and Hinshelwood, C. N., _The Mechanism of the Hydrogen-Oxygen Reaction, III. The Influence of Salts_, Proc. Royal Soc. London, Vol. 185, Series A, 376, April 1946.

11. Friedman, R., and Levy, J. B., Inhibition of Opposed-Jet Methane-Air Diffusion Flames, The Effects of Alkali Metal Vapors and Organic Halides, Atlantic Research Corporation, 31 December 1962.

12. Laffitte, P., and Bouchet, R., "Suppression of Explosion Waves in Gaseous Mixtures by Means of Fine Powders," Seventh Symposium on Combustion, 504, Butterworths, 1959.

13. Price, F. P., "First and Second Pressure Limits of Explosion of Diborane-Oxygen Mixtures," J. Amer. Chem. Soc., Vol. 72, 5361, December 1950.

14. Whatley, A. T., and Pease, R. N., "Observations on Thermal Explosions of Diborane-Oxygen Mixtures," J. Amer. Chem. Soc , Vol. 76, 1997, April 1954.

15. Roth, W., A Study of the Explosive Oxidation of Diborane, Rensselaer Polytechnic Institute, Doctoral Dissertation, May 1954.

16. Roth, W., and Bauer, W. H., "The Explosive Oxidation of Diborane," J. Phys. Chem., Vol. 60, 639, May 1956.

17. Fehlner, F. P., and Strong, R. L., "The Reaction Between Oxygen Atoms and Diborane," J. Phys. Chem., Vol. 64, 1522, October 1960.

18. Bragg, J. K., McCarty, L. V., and Norton, F. J., "Kinetics of Pyrolysis of Diborane," J. Amer. Chem. Soc., Vol. 71, 2134, May 1951.

19. Ludlum, K. H., The Oxidation of Tetraborane, Rensselaer Polytechnic Institute, Doctoral Dissertation, December 1960.

20. Snyder, A. D., Explosive Reaction of Decaborane-Oxygen Mixtures, Rensselaer Polytechnic Institute, Doctoral Dissertation, June 1957.

21. Baden, H. C., Bauer, W. H., and Wiberly, S. E., "The Explosive Oxidation of Pentaborane," J. Phys. Chem., Vol. 62, 331, March 1958.

22. Schalla, R. L., Spontaneous Ignition Limits of Pentaborane, NACA, RM E55B03, January 1957.

23. Parker, W. G., and Wolfhard, H. G., "Properties of Diborane Flames," Fuel, Vol. 35, 323, 1956.

24. Kurz, P. F., "Influence of Diborane on Flame Speed of Propane-Air Mixtures," Ind. & Engr. Chem., Vol. 48, No. 10, 1863, October 1956.

25. Berl, W. G., and Dembrow, D., "Twin Flames," Nature, Vol. 170, 367, August 1952.

26. Berl, W. G., Gayhart, E. L., Maier, E., Olsen, H. L, and Renich, W. T., "Determination of Burning Velocity of Pentaborane-Oxygen-Nitrogen Mixtures," Combustion & Flame, Vol. 1, 420, 1957.

27. George, P. D., "Qualitative Effect of Extinguishing Agents on Burning Diborane," Ind. & Engr. Chem., Vol. 46, 1709, 1954.

28. Olin Mathieson Chemical Corporation, Pentaborane, Technical Bulletin LF-202, June 1960.

29. Callery Chemical Company, Pentaborane, Technical Bulletin CT-1300, October 1961.

30. Carpenter, R. A., "Recent Advances in Boron Technology," ARS Journ., Vol. 29, 8, January 1959.

31. Reaction Motors Division, Thiokol Chemical Company, A Study of Stabilized Pentaborane, RMD-255F, 1959.

32. O'Donovan, J. T., and Fristrom, R. M., Research Study on HEF Fire Fighting, Applied Physics Laboratory, CF-3001, September 1962.

33. Stock, A., Hydrides of Boron and Silicon, Cornell University Press, 1933.

34. Hurd, D. T., An Introduction to the Chemistry of the Hydrides, John Wiley, 1952.

35. Rothberg, S., Colbourn, J. L., and Salvatore, R., "Toxicity and Personal Decontamination of Boron Hydride Propellant Fuels," Jet Propulsion, Vol. 28, 762, November 1958.

36. Gaydon, A. G., and Wolfhard, H. G., Flames, Chapman and Hall, 1960.

37. Potter, A. E., Heimel, S., and Butler, J. N., "Apparent Flame Strength," Eighth Symposium on Combustion, Williams and Wilkins, 1962.

38. Hottel, H. C., and Hawthorne, W. R., "Diffusion in Laminar Flame Jets," Third Symposium on Combustion, Flame and Explosion Phenomena, Williams and Wilkins, 1949.

39. Wohl, K., Gazley, C., and Kapp, N. M., "Diffusion Flames," _Third Symposium on Combustion, Flame and Explosion Phenomena_, Williams and Wilkins, 1949.

40. Webber, W. T., "Spray Combustion in the Presence of a Travelling Wave," _Eighth Symposium on Combustion_, Willams and Wilkins, 1962.

41. Cramer, F. B., _The Onset of Detonation in a Droplet Combustion Field_, Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, California, 1962.

42. Shapiro, A. H., _The Dynamics and Thermodynamics of Compressible Fluid Flow_, Vol. 1, Ronald Press, 1953.